R & D NOTES

Mechanism of Carbon Gasification—Conformation of Etch Pits on Graphite Surface With and Without Tungsten Catalyst

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The kinetics of gas-carbon reactions has been a research area of long standing and presently growing interest to chemical engineers since Hottel and coworkers studied the rates of combustion of a hanging graphite ball (Tu et al., 1934). The voluminous literature published prior to 1959 has been discussed by Walker et al. (1959). Reviews of more recent papers may be found in Essenhigh (1981), Johnson (1981), and Yang and Steinberg (1977).

The mechanisms of the reactions of CO_2 and H_2O on carbon surface have been reasonably understood. These reactions have been demonstrated to follow the Langmuir-Hinshelwood, or Langmuir-Hinshelwood-Hougen-Watson, mechanism since the work done by the Hinshelwood school (Walker et al., 1959). The reaction between carbon and O_2, on the other hand, is relatively less understood although more extensive studies have been done on this reaction. The rate of these reactions have been done on this reaction. The rate of these reactions have been conventionally measured on a per surface area or per weight of carbon basis.

It was the development of the etch-decoration transmission electron microscopy technique primarily by Hennig (1966) which made it possible to study the carbon gasification kinetics on an atomic scale and to measure the rates on a per active carbon site basis. It has been known, by using this technique, that for the three aforementioned carbon gasification reactions the active sites on a graphitic carbon are the carbon atoms on the edges and defects. Other new insights on the kinetics and mechanism of these reactions obtained by this technique were summarized by Thomas (1970).

In the past decade, except for the development of and the interesting studies done on catalyzed gas-carbon reactions by the controlled atmosphere electron microscopy (CAEM) technique by Baker (1979), the only studies on the kinetics and mechanism of gas-carbon reactions using electron microscopy have been done by the authors. It has been shown that the surface diffusion of chemisorbed oxides is important in the carbon-oxygen reaction on surfaces with isolated active sites (Yang and Wong, 1981a), and the surface diffusion contribution to the rate has been quantitatively characterized by an inert gas flush technique (1981b,c).

Oxidation of lattice vacancies in the exposed basal plane of graphite leads to the development of a circular etch pit. Circular pits one layer deep have been unequivocally seen with the gold-decoration/transmission electron microscopy (TEM) technique as exemplified by Figure 1. The etchant gases O_2, CO_2 (Feates, 1968) and H_2O (Montet and Myers, 1968) all lead to circular pits on a clean surface. However, we have found that when tungsten is present on the surface, all are consistently hexagonal in shape. Furthermore, the rate of pit expansion is increased or catalyzed by tungsten, and the amount of tungsten dictates the increase as well as the sharpness of the corners of the hexagon. In this note, we report our findings on the catalytic effects on the C-O_2 reaction by tungsten and suggest a general mechanism by which different conformations of pits arise.

The experimental technique of etch-decoration has been fully described (Hennig, 1966). We will briefly describe the technique and experimental conditions, along with our methods of introducing tungsten on the graphite surface. A piece of single crystal natural graphite (from Ticonderoga, NY) is cleaved to a thickness less than about 800 Å (for electron transmission). The sample is then etched (or reacted) with O_2 (0.2 atm O_2 in Ar) at 680°C for a period of 5 to 30 min. The residual vacancies on the surface of the basal plane, or (0001) face, are expanded into pits one atomic layer deep. Gold is then evaporated under vacuum [2×10^{-6} torr (Pa = torr $\times$ 133)] onto the surface, which is maintained at 250°C to assist migration and subsequent nucleation of the gold atoms onto the edges of the pits. The amount of gold evaporated is controlled to give about a monolayer deposition. As a result of preferential nucleation on the edge carbon along the steps of the pits, gold nuclei (which are electron-opaque) surrounding the pits are seen under a TEM. Furthermore, from the pit expansion rate, one may calculate the rate of carbon removal per edge carbon atom. For tungsten deposition, two methods have been employed, both involved depositing tungsten on the surface prior to oxidation. In one, the graphite flake, before cleavage, was heated in a tungsten holder *in vacuo* (2×10^{-6} torr) at near 1,800°C for 12 h (hour). The other method involved heating the cleaved sample in the tungsten holder at above 1,300°C *in vacuo* for 12 h. With either method, tungsten

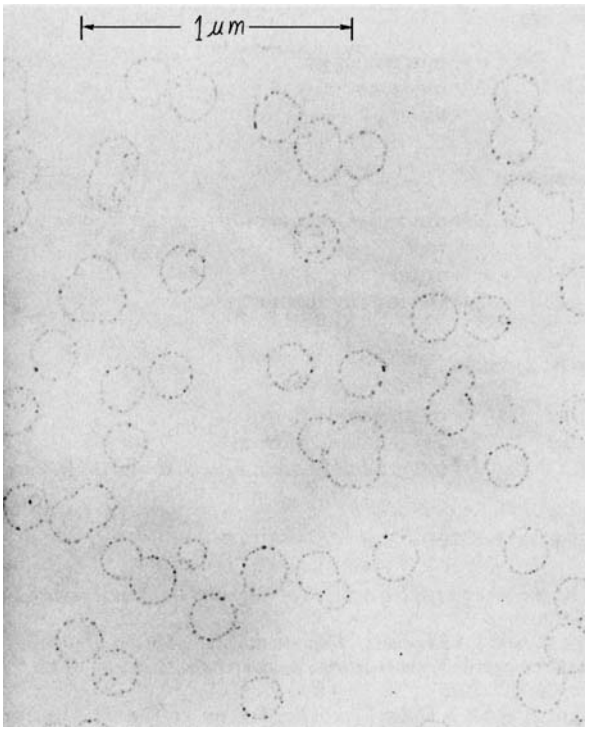

Figure 1. Transmission electron micrograph of the surface of graphite after oxidation for 20 min at 680°C with 20% O_2 (in 0.8 atm Ar), followed by gold decoration.

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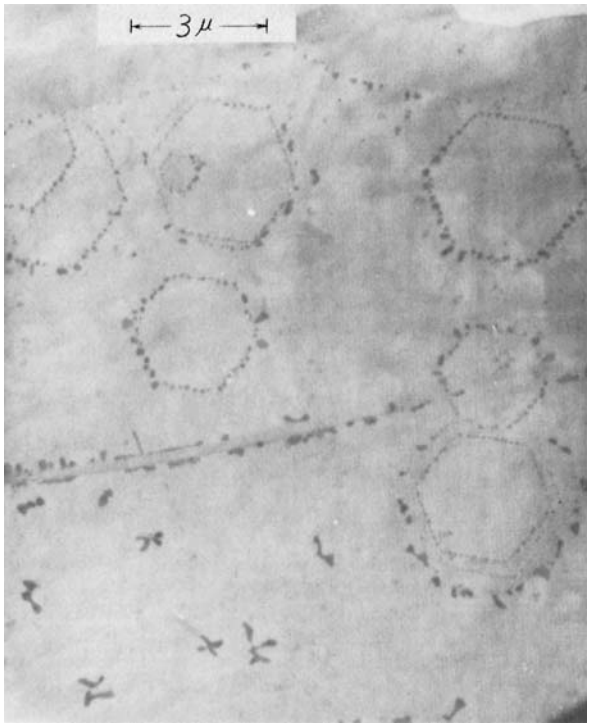

Figure 2. Same as in Figure 1, except that tungsten was deposited on the surface prior to oxidation and that the reaction time was 15 min.

was detected on the cleaved graphite surface by an energy dispersive x-ray analyzer attachment in a scanning electron microscope. A peak at 8.396 keV (kilo electron volt) on the $L\alpha$ band showed the presence of tungsten. In the first method, tungsten probably intruded into graphite through glissile dislocations which also provided the weakest parts for cleavage. The contacting points between the tungsten and the carbon flake were on the edges. The tungsten thus deposited was most likely in a carbided form where carbon was supplied from the edges (Toth, 1971).

The tungsten-deposited and cleaved crystals were oxidized in 0.2 atm O_2 (in Ar at 1 atm) at 680°C for times ranging 5–30 min,

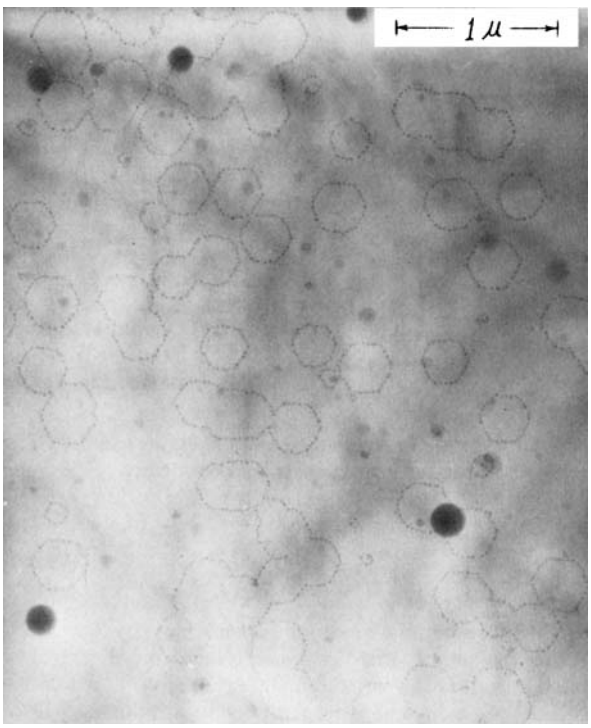

Figure 3. Same as in Figure 2, except that less tungsten was deposited on the surface.

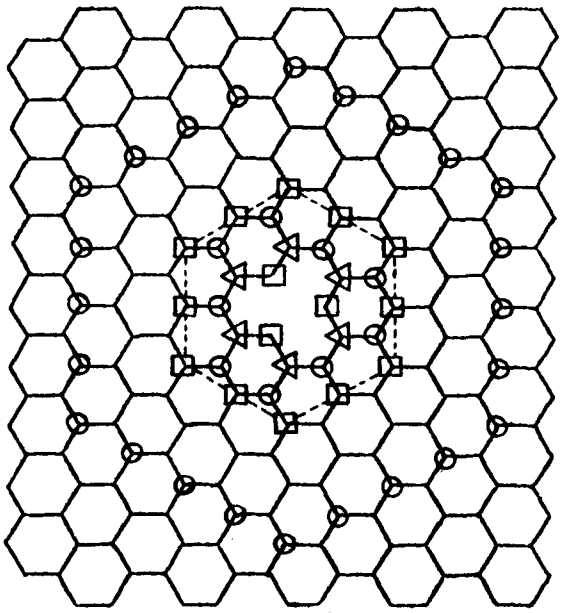

Figure 4. Conformation of etch pit from a single vacancy in the early development. The symbols denote surface atoms at each step during pit expansion.

and subsequently gold-decorated and examined under TEM. In all samples, decorated hexagonal pits were seen, with no circular pits whatever. The hexagonal pits had the same orientation, and the rates calculated from the sizes of the pits were all higher than those calculated from circular pits created under the same conditions on a clean surface.

Figure 2 shows a typical result for a sample on which tungsten was deposited by intrusion at the higher temperature before cleavage. Figure 3 is for a sample where tungsten was deposited by direct contacting the cleavage face on tungsten at the lower temperature. The shapes of tungsten/carbide were quite different for the two cases. The "butterflies" and irregularly shaped dots on Figure 2 are probably tungsten/carbide, whereas in the latter case, they are definitely in the form of thin discs with diameters up to about 2,000 Å. It has been further observed that the sharpness of the hexagons and the corresponding rate of carbon gasification depend directly on the amount of tungsten deposited on the surface. The rate (or turnover frequency from Figure 2 is 19.2 atoms/atom (active site)/s; the corresponding rate on a clean surface where circular pits are formed is 3.3 atoms/atom/s (Yang and Wong, 1981 a-c). The latter rate is taken for the same vacancy density since we have shown that the rate is strongly dependent on the vacancy density. The rate from Figure 3 is 2.8 atoms/atom/s, as compared with the corresponding rate on a clean surface of 0.65 atom/atom/s as shown in Figure 1. (The ring densities on Figures 1 and 3 are approximately equal.) The enhancement of rate by tungsten carbide is less in the latter case, which also gives less sharp hexagons. To understand these results, the discussion must be made in conjunction with the question of how circular pits are formed on a clean surface, which still remains unresolved.

The origin of etch pits is largely from single vacancies, as demonstrated by Dawson and Follett (1963). Here we define surface atoms as the ones with an unbonded or free-sp^2 electron. These atoms are more active than the "bulk" atoms. Figure 4 illustrates the early development of the etch pit starting from a single vacancy. It is seen that after three layers of surface atoms are removed, the pit is already bounded by the surface atoms which form a hexagon. Further removal of the active surface atoms will expand the hexagon. To form a circular pit, on the other hand, will require additional removal of atoms near the middle of each side, or to make the hexagon rounded. Once it is rounded, continued removal of surface atoms, layer-by-layer, will lead to a larger circular pit. In the early stage of pitting, the O_2 (or CO_2 and H_2O) molecule is not small compared to the pit, and hence removal of the corner

atoms is relatively hindered due to steric reasons. One would expect that O_2 develops a rounded pit in the early stage which leads to a circular pit. When tungsten carbide is present on the surface, 0 atoms are expected to be present near the surface because tungsten carbide is effective in dissociating O_2. It might involve an oxygen spillover process similar to the hydrogen spillover phenomenon (Levy and Boudart, 1974). With 0 atoms the steric factor should not be important and indeed hexagonal pits are formed by 0 atoms from the gas phase (Wong et al., 1983). A spillover mechanism was earlier proposed for chromia catalyzed carbon oxidation (McKee, 1970; Baker, 1981). A further for the tungsten being in the form of tungsten carbide is that any metallic tungsten would have been oxidized, at least on the surface layers, under our conditions, and tungsten oxide behaves very differently in its catalytic activity. Our results on WO_3 catalyzed carbon oxidation will be reported shortly.

The orientation of the hexagonal etch pits has been determined by in situ electron diffraction using TEM. All sides of the pits are in the $\langle 1,0\bar{1}0\rangle$ direction i.e., they are zigzag surfaces, which is the orientation shown in Figure 4, as well as the orientation of the hexagonal pits etched by 0 atoms (Wong et al., 1983). Deep pits created by catalyst particles are mostly circular, but in a few cases hexagonal, e.g., by Fe_2O_3 (Thomas, 1965; McKee, 1970). The mechanism proposed here may also be operative in deep pits formation.

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Approximate Global Rates: Reactions Affected by Diffusion and Chemical Deactivation

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INTRODUCTION

Global rates have been obtained for reactions affected by both diffusion and chemical deactivation (Lee and Butt, 1982a). These global rates were used to simplify the design of heterogeneous reactions. These results, however, were restricted to the limiting cases of uniform and shell-progressive deactivation. In this paper, we remove this restriction and obtain global rates for a general case of deactivation.

When a pellet of uniform catalytic activity is deactivated, the outer surface loses the activity more rapidly than the inner part due to its direct exposure to poisoning species, resulting in a nonuniform pellet with its activity increasing monotonically toward pellet center. For such a pellet, the flux at the outer surface can be accurately approximated (Lee, 1981a) by:

$$-D_e \left.\frac{dc}{dx}\right|_{\text{surface}} \equiv D_e \bar{P} \simeq \left[2\bar{f} D_e \int_{C_c}^{C_b} r_c(C)dC\right]^{1/2} \qquad (1)$$

provided that a certain condition is met. Here the function representing the activity distribution resulting from deactivation is denoted by f and the overbar denotes evaluation at the pellet surface. The bulk-fluid and pellet center concentrations are denoted by C_b and C_c, respectively. For the diffusion-limited reactions being considered, the pellet center concentration can be set at zero.