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Catalysis of Carbon Oxidation by Transition Metal Carbides and Oxides

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The technique of etch decoration/transmission electron microscopy has been employed to study the catalysis of the carbon–oxygen reaction by seven group VB and VIB metal carbides and oxides. Turnover frequencies for carbon gasification were measured at 680°C from the monolayer pit expansion rate on the basal plane of single-crystal graphite, with and without catalyst particles deposited on the surface. Among the catalysts used in this study, only MoO_3 followed the well-established mode of channeling, while all others catalyzed the reaction at the edges of the etch pits which were distant from the catalyst by apparently a long-range action. The etch pits formed in the presence of carbides (WC, TaC, and Mo_2C) were all hexagonal, unlike the uncatalyzed reaction in which pits were circular, and the edges of the hexagonal pits were composed of the zigzag $\{10\bar{1}0\}$ faces. These pits were similar to those created directly by atomic oxygen. The results suggested that the transition metal carbides served as dissociation centers and dissociation was followed by spillover and reaction on the edges of the pits. Deformed circular pits were formed in the presence of the oxide catalysts (Cr_2O_3, WO_3, and Ta_2O_5), and the oxide catalyst particles disintegrated and dispersed on the surface. Because the reaction temperature was near or above the Tammann temperatures, it appeared that the catalysts dispersed by emission of molecular species or clusters which migrated on the basal plane of graphite and were subsequently trapped on the edges of the etch pits. Gasification of the edge carbon atoms was thus catalyzed by the trapped catalyst through direct contacts.

INTRODUCTION

Two major mechanisms have been proposed for the catalyzed gasification of carbon: oxygen transfer and electron transfer. In the oxygen transfer mechanism, the solid catalyst forms intermediate(s) in the oxidizing gaseous atmosphere and the intermediate(s) oxidizes the carbon in its vicinity. In so doing the catalyst returns to its original state and the cycle continues. This mechanism has long been proposed (*1*) but has received much credence only recently from the work of McKee (*2*). The electron transfer mechanism, first proposed by Long and Sykes (*3*), stipulates that the carbon–carbon bonds attached to the edge or surface carbon are weakened because the carbon matrix transfers an electron to the metal ion in the catalyst, and thereby facilitates the gasification of the edge carbon. This mechanism has been used to explain many catalyzed reactions of carbon by O_2, CO_2, and H_2O (*2*, *4*). Other mechanisms fundamentally different from these two have also appeared in the literature. Holstein and Boudart have proposed a "catalyzed carbon–carbon bond breakage" mechanism for carbon gasification by H_2 (*5*), H_2O, and CO_2 (*6*) catalyzed by platinum. This mechanism stresses the ability of the catalyst to directly break the carbon–carbon bonds without the participation of the adsorbed gas. A modification of the electron transfer mechanism in terms of intercalation was proposed for the carbon–oxygen reaction catalyzed by alkali metal compounds (*7*). The electronic configuration of the intercalated compounds is thought to enhance chemisorption and thus facilitates the reaction. A variation to the oxygen transfer mechanism has been proposed by Mims and Pabst to interpret the alkali salt catalyzed C–H_2O reaction (*8*). A surface phenoxide group,

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=COK, is thought to be the active site for carbon gasification. This surface group is an activated and stable group which facilitates a high dispersion of the catalyst. Evidence of the existence of this group and its role in the reaction have been shown and discussed by several authors (*9–11*). It is proposed that gasification of this active site proceeds by a rapid reversible oxidation followed by a slower decomposition step. Still another proposed mechanism is the somewhat more controversial one of dissociation–spillover. The catalyst in contact with carbon serves in dissociating the gas molecules into atomic species which then migrate on the carbon surface until reaching an active carbon site where gasification takes place. Attempts have been made in employing this mechanism to interpret the features of the C–H_2 reaction catalyzed by platinum (*5, 12*), and the C–O_2 reaction by Cr_2O_3 (*13, 14*). Convincing evidence, however, has been found for this mechanism in our study of the C–O_2 reaction catalyzed by tungsten carbide (*15*).

Clearly, there is no single mechanism which can describe all catalyzed carbon gasification reactions. It is likely that different mechanisms may be dominating for gasification by different gases, and for the same gas at different temperatures.

The behavior of catalyst particles during the catalyzed carbon gasification is rather unique in that the particles form channels or localized, deep pits on the carbon substrate. This phenomenon has been revealed and studied on the basal plane of graphite single crystals, using etch-decoration electron microscopy (*16*), controlled atmosphere hot stage optical microscopy (*13, 17*), and electron microscopy (*18, 19*). With a few exceptions, all channeling studies have been done with the carbon–oxygen reaction, in the temperature range of 500–800°C. Over 30 metals and metal oxides, mostly transition and noble metals, have been studied (*13, 14, 16–19*). Most of the catalyst particles form channels while a few form pits or both channels and pits. There are, however, several catalysts which do not form channels or pits, yet they do catalyze the oxidation reaction. These nonchanneling, nonpitting catalysts are the subjects of this study. Among the nonchanneling, nonpitting catalysts are Ta_2O_5 ((*17*), but reported as nonactive in Ref. (*13*)), Cr_2O_3 (*13, 14*), and WC (*15*).

The origin of the particle channeling phenomenon is still not understood. Baker has been successful in correlating the speed of channeling with size and Tammann temperature (*20*). Channeling occurs either in preferred crystallographic directions of the graphite surface or in random directions. Preferential wetting of the zigzag face ($\langle 11\bar{2}0\rangle$ direction), because of the higher interfacial tension, has been attributed to the channeling in the said direction by nickel particles in the C–H_2 reaction (*21*). However, wetting cannot be used to explain the channeling of gold in the C–O_2 reaction where the preferred direction of channeling is zigzag ($\langle 11\bar{2}0\rangle$ direction) in dry oxygen, and armchair ($\langle 10\bar{1}0\rangle$ direction) in moist (2.5% H_2O) oxygen (*16*).

In this study, we applied the etch decoration/transmission electron microscopy technique (EDTEM) to examine the mechanism of the action of the nonchanneling, nonpitting catalysts on the carbon–oxygen reaction. The catalysts used in this study included Cr_2O_3, WO_3, Ta_2O_5, MoO_3, WC, TaC, and Mo_2C.

EXPERIMENTAL

It has been well known since the 1940's that heterogeneous nucleation occurs at dislocations on the solid surface, and the decorated dislocations can be examined by optical microscopy. Using the transmission electron microscope (TEM), Bassett in 1958 (*22*) was able to show the presence of monoatomic steps (2.8 Å) on the cleaved surface of rock salt by depositing a metal vapor on the surface. Bassett's work was immediately followed by the ingenious development of the etch decoration/transmission electron microscopy technique and the use of the technique to study carbon gasification kinetics and mechanism by Hennig (*23*), Thomas (*24*), Feates (*25*), and others.

The EDTEM technique, described in details by Hennig (*23*), 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 (in our case, 20% O_2 in argon at 1 atm) which expands the surface vacancy to create a pit one atomic layer deep, decorating the edge of the pit with gold nuclei, and examining with TEM. The radius 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 rate of removal of carbon atoms per active site, or the turnover frequency. Consequently the technique is capable of producing a wealth of fundamental information on the mechanism of both uncatalyzed and catalyzed gas–carbon reactions. However, the technique is rather temperamental and is sensitive to a large number of factors which are not fully understood (*23, 26*). Nevertheless reproducible and consistent results can be obtained (*26*) which provide a first step in developing a fundamental understanding of gas–solid reactions.

Prior to etching the sample with reactant gases, it was found necessary (*26*) to purge the sample with an inert gas (Ar in our experiments) at 650°C for a prolonged period of time, at least 10 hr. Without this step, the etched sample could not be successfully gold-decorated. This was probably caused by preferred nucleation of gold atoms on the tightly bound species on the graphite surface as numerous small gold nuclei were seen. The prolonged purge ensured the desorption of these species.

For catalyzed reaction studies, the cleaved single-crystal graphite was coated with catalyst particles prior to etching or reaction. The catalysts used in this study were Cr_2O_3, WO_3, Ta_2O_5, MoO_3, WC, TaC, and Mo_2C (Alfa Products, Danvers, Mass.). All of the catalysts with the exception of Cr_2O_3, which was deposited as chromium acetate and oxide solutions, were insoluble in water and were dispersed on the cleaved graphite as water slurry. The concentrations of the slurries and solutions were made to correspond to 0.1 *M*. The particle sizes were predominantly near 0.2 μm. The slurry or solution was applied to the cleaved graphite surface by a syringe, and the sample was subsequently dried. It should be noted that this method of coating the samples in conjunction with the small graphite basal plane area (which varied from sample to sample) did not allow a quantitative determination of the amount of catalyst deposited. It was also difficult to reproduce the amount of catalyst loading. Therefore no attempt was made to measure the activation energy and the gas-concentration dependence. However, the catalyst particles were visible in TEM. The rates reported in this study were the expansion rates of the monolayer pits which were at distances away from the catalyst particles. The catalyzed rates thus varied from sample to sample due to different amounts of catalyst deposited. Nevertheless, the mechanisms of the catalyzed reactions reported here, which do not depend on the amount of the catalyst, are conclusive.

RESULTS AND DISCUSSION

Turnover Frequency Calculation

For the uncatalyzed carbon–oxygen reaction, linear relationships were obtained between the size of etch pits and reaction time (*23–26*). The linearity indicates that the turnover frequency is constant during the reaction. Thus the rate of expansion of pit radius (R), dR/dt, may be calculated from a single experiment. The turnover frequency can then be evaluated as

$$r\left(\frac{\text{atoms gasified}}{\text{edge atom} \cdot \text{s}}\right) = \frac{\rho_{0001} 2\pi R dR/dt}{\rho_{11\bar{2}0} 2\pi R H} \quad (1)$$

where $\rho_{0001} = 0.377$ C/Å^2, $\rho_{11\bar{2}0} = 0.140$ C/Å^2, and H = step height = 3.35 Å.

Figure 1 shows the gold-decorated etch pits on a sample with no catalyst. The turnover frequency from this figure was 0.6 1/s. The pits for the uncatalyzed reaction were circular loops. The activation energy for the reaction was 35 kcal (*24, 25*).

With catalysts deposited on the surface, as mentioned in the experimental section, it was not possible to reproduce the amount and the dispersion of the catalyst particles from sample to sample. Thus no effort was made to check the linearity of the pit size–time relationship. The turnover frequencies reported in this study were therefore "overall" values, i.e., the average rate over the entire period of reaction. Nonlinear behaviors may be possible. For example, an "incubation" period was reported for the channeling of KOH particles in the carbon–steam reaction at 500°C (*27*). However, the overall rates were used to obtain insights into the catalytic mechanisms, and no quantitative calculations on the individual steps involved in the mechanisms were attempted at this point.

Oxidation Catalyzed by Carbides

No studies have been reported on the catalysis of carbon gasification by transition metal carbides. The three carbides investigated here, WC, TaC, and Mo_2C all increased the overall pit growth rate substantially. More important, the etch pits were all hexagonal in shape, and the sides of the pits were composed of the zigzag face ($\{10\bar{1}0\}$) as identified by selected area diffraction using TEM. Another important feature of the transition metal carbide-cata-

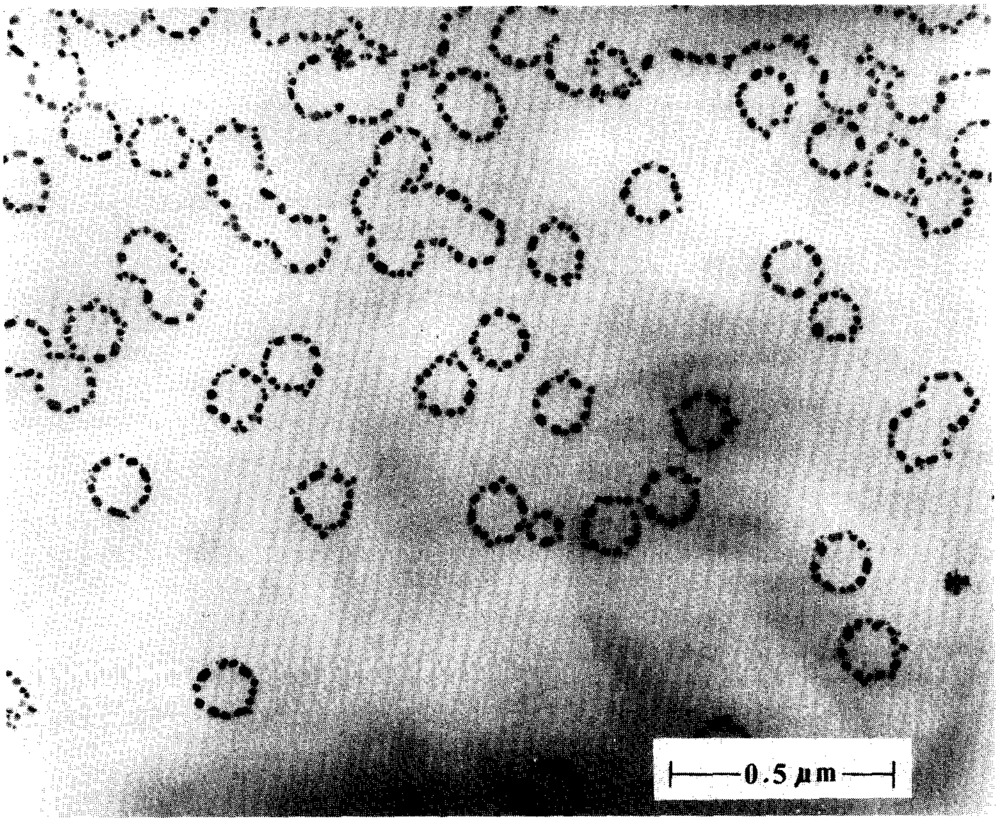

FIG. 1. Transmission electron micrograph of the basal surface of graphite after oxidation for 25 min at 650°C with 0.2 atm O_2 (with 0.8 atm Ar), followed by gold decoration.

lyzed reaction was that no channeling or pitting was observed. The catalyst particles were at distances away from the etch pits. The catalysis was apparently due to a remote-action mechanism.

The pits produced on the basal plane by WC-catalyzed carbon–oxygen reaction are shown in Fig. 2. The overall turnover frequency calculated from this figure was 6.2 atoms/atom/s. (In this calculation $\rho_{11\bar{2}0}$ in Eq. (1) was replaced by $\rho_{10\bar{1}0}$.) An uncatalyzed sample oxidized under the same conditions would have a turnover frequency in the range of 0.7 to 1.2 atoms/atom/s. The turnover frequency for the uncatalyzed oxidation reaction is dependent on the density of pits, or the active site density, as demonstrated previously (*28, 29*). Dispersed large particles of tungsten carbide were clearly visible in TEM but not shown in the area covered by Fig. 2. The sizes of the pits produced by WC-catalyzed reaction were uniform for a given area of the graphite surface while varied slightly for different areas of a given sample. Sizable differences were observed from sample to sample due to the different quantities of catalyst deposited on each sample.

The behavior of tantalum carbide, TaC was similar to that of tungsten carbide. Hexagonal pits of the same orientation were produced during oxidation, as shown in Fig. 3. The overall turnover frequency from Fig. 3 was 12.5 atoms/atom/s. The behavior of molybdenum carbide was rather peculiar, as shown in Fig. 4, in that the hexagonal pits were uniformly deformed. The pits had the same orientation as those produced by WC and TaC, i.e., the walls of the hexagonal pits were composed of the zigzag face of graphite. However, the hexagons produced by Mo_2C appeared to be uniformly elongated. The turnover frequency was estimated as 12.5 atoms/atom/s. The catalyzed rates are summarized in Table 1.

Our recent experiments with graphite gasification by atomic oxygen have shown that the resultant monolayer etch pits were hexagonal, and the orientation of the hexagonal pits was that with the zigzag faces (*30*). Thus the hexagonal shape of the etch pits, with the zigzag orientation, for the transition metal carbides catalyzed oxidation is indicative of attack by atomic oxygen. The transition metal carbides have electronic structures similar to that of platinum and possess catalytic activities for dissociating O–O and H–H bonds (*31, 32*). Therefore it is likely that the transition metal carbides act as dissociation centers for molecular oxygen generating atomic oxygen or surface oxide species which subsequently diffuses across the basal plane of graphite and reacts at edges of the monolayer pits. The reason for atomic oxygen forming hexagonal pits with the zigzag orientation as opposed to molecular oxygen forming circular pits is likely a steric one, which has been described previously (*15*). The reason for the uniform elongation of the pits formed by molybdenum carbide remains unknown.

At this point, the possibility of the surface of carbides being oxidized during the reaction is rather uncertain. The reaction time was short, i.e., 7 to 10 min. The bulk was definitely not oxidized as the bulk oxide catalysts would give entirely different results as shown in the next part of the paper. Furthermore, since the catalyst surface must be predominantly carbidic in the initial period of the reaction, and the conformation of the etch pits, e.g., hexagonal vs circular, depended on the initial period of pit formation, the carbidic surface was most likely the active species for the dissociation–spillover mechanism in the initial period. However, the possibility of an oxidized surface being the active species in the later period of reaction cannot be ruled out.

Catalysis by Transition Metal Oxides

Except MoO_3, a number of common features have been observed for the catalysis of the carbon–oxygen reaction by the transition metal oxides used in this study, as summarized below. Like their counterpart carbides, no channels or deep pits were

FIG. 2. Hexagonal etch pits with the zigzag $\{10\bar{1}0\}$ faces produced on the basal plane of graphite by oxidation at 680°C in 0.2 atm O_2 for 10 min with WC catalyst. WC particles (0.2-μm size) are not shown in the figure.

FIG. 3. Hexagonal pits with zigzag orientation produced on the basal plane by oxidation at 680°C in 0.2 atm O_2 for 10 min with TaC catalyst (particles not shown in figure).

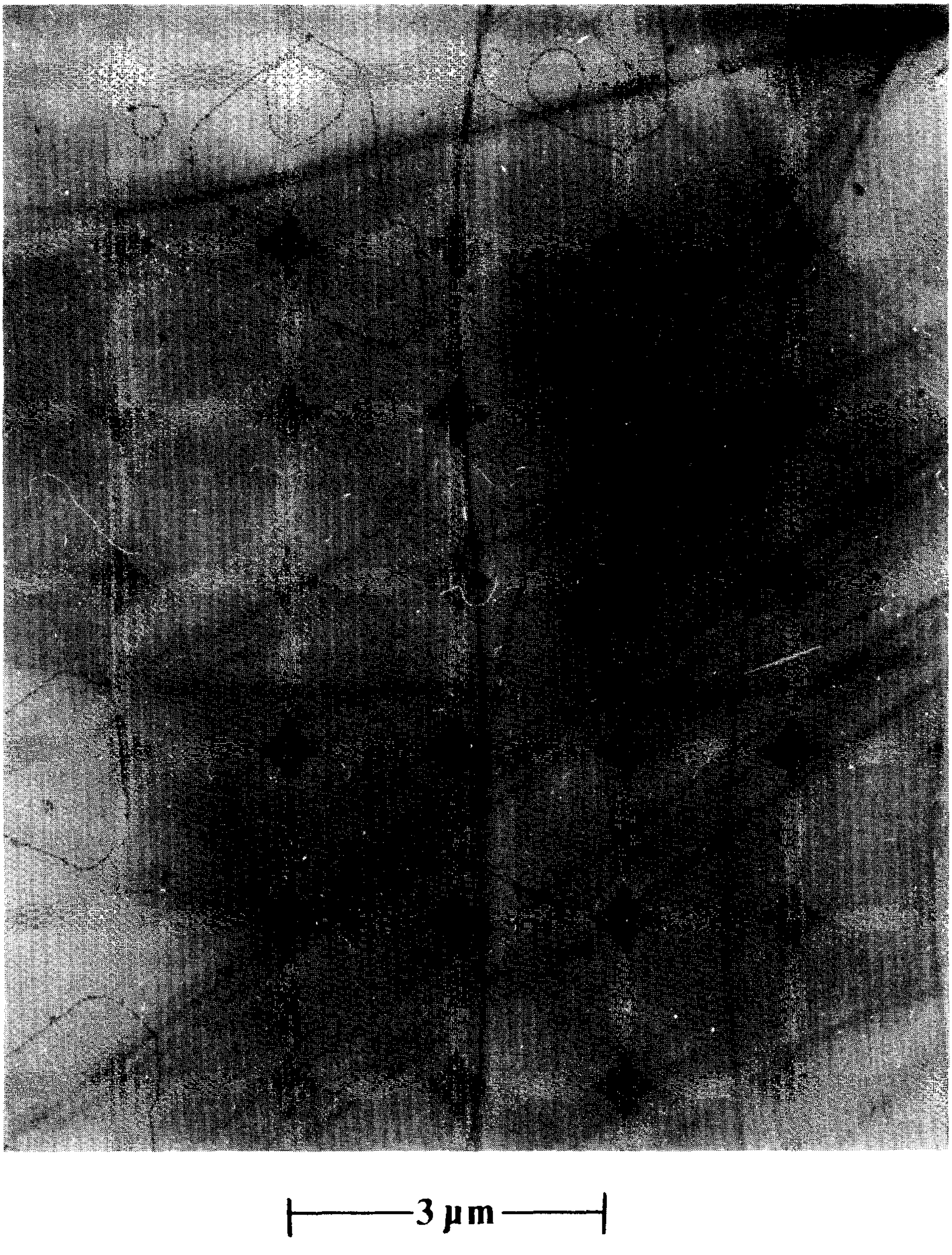

FIG. 4. Elongated hexagonal pits produced by oxidation at 680°C in 0.2 atm O_2 for 10 min with Mo_2C catalyst (particles not shown in figure).

TABLE 1

Overall Turnover Frequencies for Carbon Oxidation (over 7–10 min reaction time) in 0.2 atm O_2 at 680°C Catalyzed by Transition Metal Carbides and Oxides

Catalyst	Overall turnover freq. (s^{-1})	Tammann temp. (°C)
WC	6.2	1325
TaC	12.5	1887
Mo_2C	12.5	1266
WO_3	15.6	635
Cr_2O_3	4.7	1135
Ta_2O_5	3.1	804
MoO_3	Formed channels	282
None	0.7–1.17	—

formed, while the monolayer pit expansion rate was increased by the catalysts by a long-range action. Unlike the carbides, the monolayer pits were deformed circular ones rather than being hexagonal, and the large oxide particles (ca. 0.2 μm) originally present on the surface had disappeared after the etching step. Furthermore, there appeared to be consistent excess gold nucleation on the basal plane of graphite.

Although comparisons between different samples were difficult because a lack of reproducibility in catalyst deposition, tungsten oxide appeared to be the most active of the transition metal oxides examined. The turnover frequency for the WO_3-catalyzed sample shown in Fig. 5 was 15.6 atoms/atom/s, as compared to the value of 0.7 to 1.2 atoms/atom/s for the uncatalyzed reaction. The etch loops produced by WO_3 were somewhat irregular, although they were not as deformed as the loops produced with Cr_2O_3 and Ta_2O_5. There was also a small amount of carbon abstraction from the basal plane leading to smaller etch pits. A sample catalyzed by Cr_2O_3 is illustrated in Fig. 6. The turnover frequency was 4.7 atoms/atom/s. Tantalum pentaoxide behaved in a somewhat more erratic manner. The etch loops formed in the presence of Ta_2O_5 were extremely deformed and nonuniform as shown in Fig. 7. The turnover frequency was approximately 3.1 atoms/atom/s. Molybdenum trioxide was the only oxide examined that behaved in the conventional mode by producing channels through graphite, Fig. 8 (*16–21*). But unlike the channeling reported in the literature, the channels produced by MoO_3 were unusually shallow; they were probably only a single layer deep judging from the merging patterns, and no particles were observed in the tips of the channels. The turnover frequencies for the transition metal oxides are listed in Table 1, along with the Tammann temperatures.

The experimental results described above and the fact that the reaction temperature (680°C) was near or above the Tammann temperatures of the catalysts suggested a mechanism in which molecular species or small clusters were emitted from the particles and were trapped on the edges of the pits, and subsequently catalyzed the reaction by direct contacts. This mechanism would be similar to the theory of emission/migration proposed for sintering of supported metal and metal oxide catalysts as reviewed recently (*33*, *34*). Such a mechanism was consistent with all the features observed. Different amounts of catalysts trapped in different areas of the pits would cause the deformation. The excessive nucleation of gold observed could be accounted for by the presence of catalyst clusters which would go undetected without gold decoration. These clusters could have been trapped by energy wells on a nonuniform surface potential on the carbon surface created by the metal oxides, consistent to the observation of stable dispersion of platinum on carbon by the added high-valence metal oxides on carbon (*35*). The cluster trapped on the pit edges could catalyze the carbon gasification by an oxygen-transfer or electron-transfer mechanism. The dispersion (and disappearance) of the catalysts could have also taken place during the prolonged inert-gas flush step (at 650°C). This phenomenon is under further study in our laboratory.

Although it was difficult to correlate the

FIG. 5. Etch loops produced by oxidation at 680°C in 0.2 atm O_2 for 10 min, with WO_3 catalyst particles initially deposited on surface.

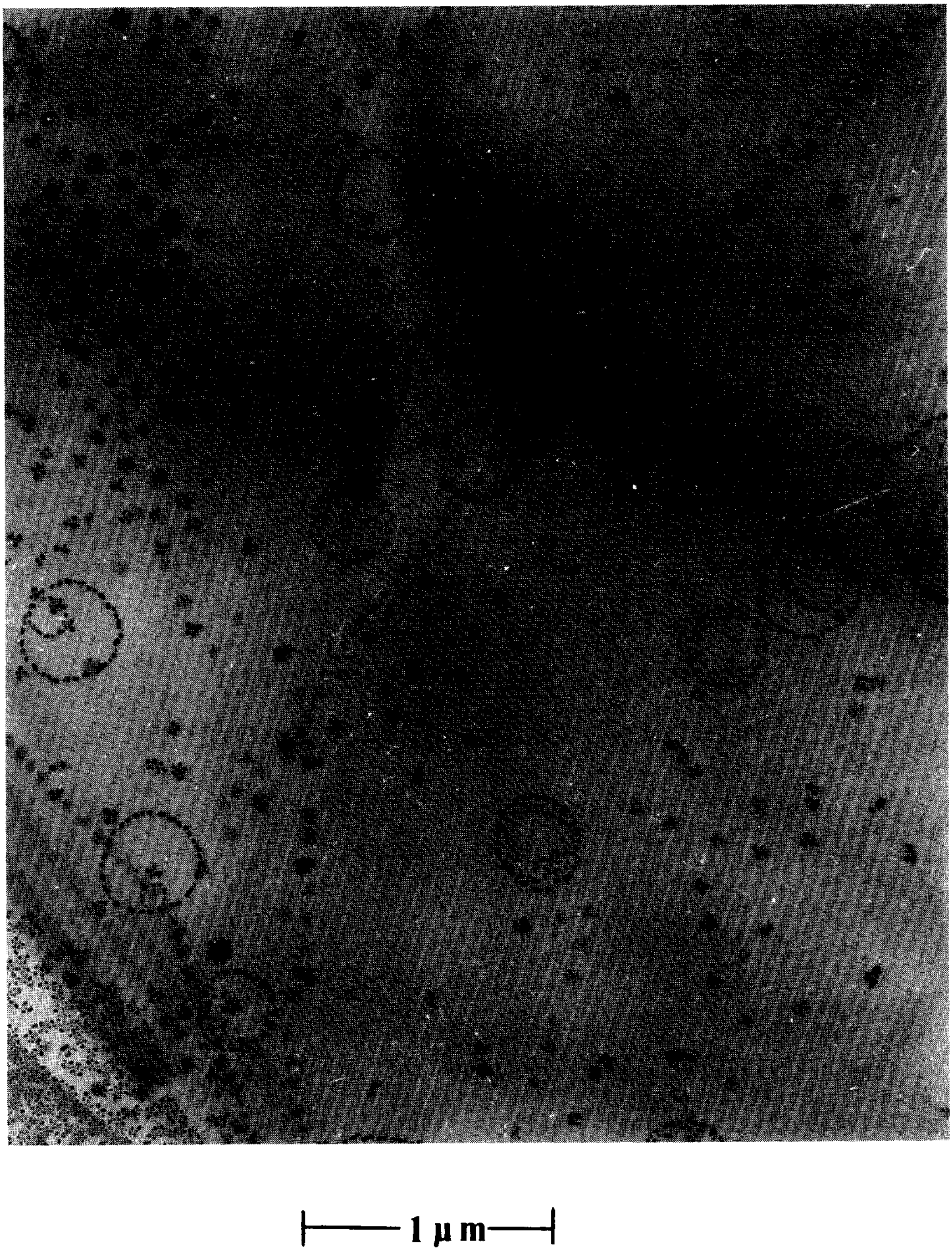

FIG. 6. Etch loops produced by oxidation at 680°C in 0.2 atm O_2 for 7 min, with Cr_2O_3 catalyst initially deposited on surface.

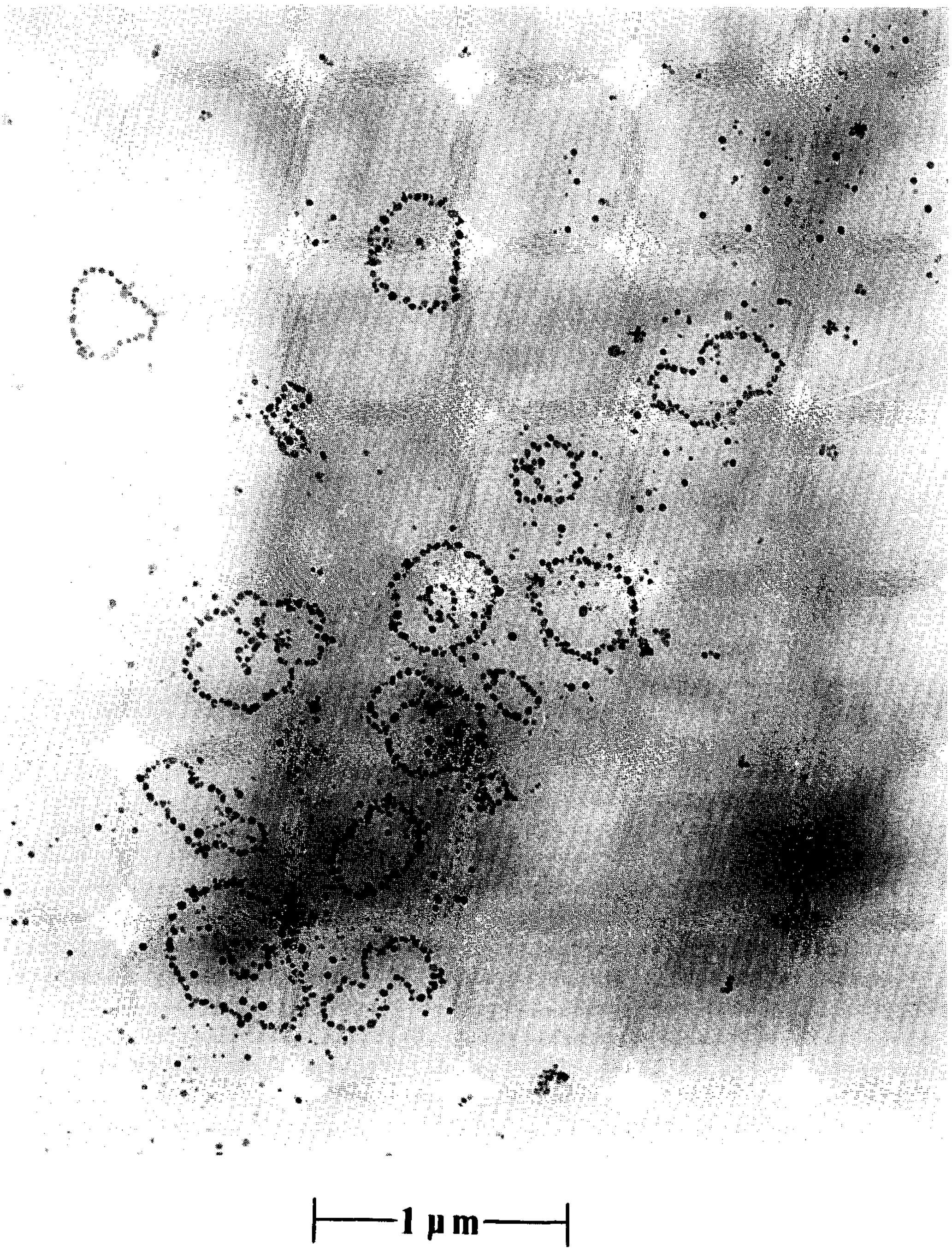

FIG. 7. Etch loops produced by oxidation at 680°C in 0.2 atm O_2 for 10 min with Ta_2O_5 catalyst initially deposited on surface. Note the formation of the severely deformed pits.

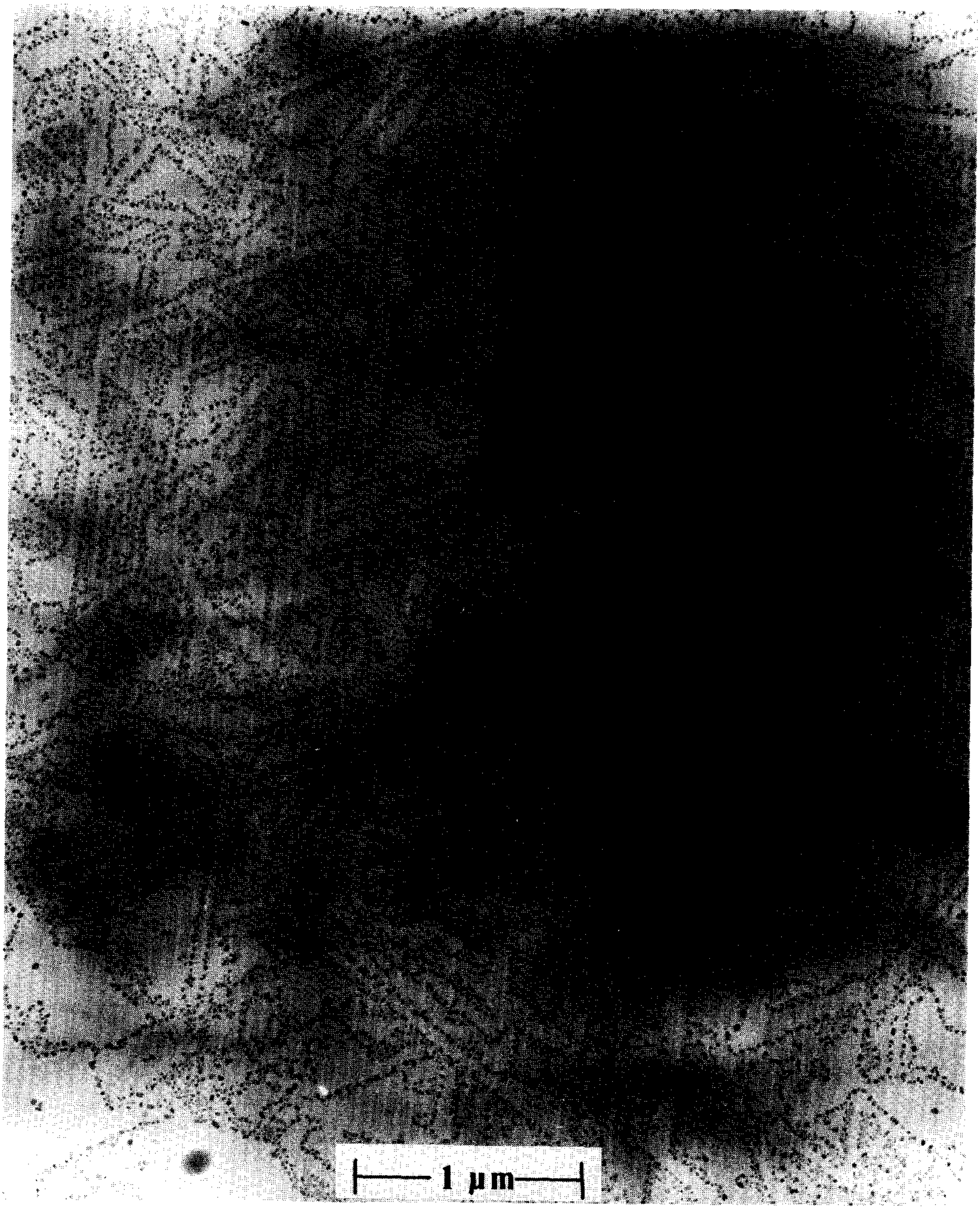

FIG. 8. Channels produced by MoO_3 catalyst on the basal plane of graphite oxidized by 0.2 atm O_2 at 680°C for 10 min.

reactivity of the catalyst because the loading could not be measured, there was a correlation between the observed turnover frequency and the uniformity of the etch pits, which was consistent with the emission/trapping mechanism. Molybdenum trioxide was the only group VI metal oxide studied that created channels. The temperature of reaction was well above the Tammann temperature (282°C). Thus the catalyst was highly mobile. As suggested by McKee (*13*) MoO_3 probably undergoes an oxygen transfer cycle at the point of contact between the catalyst and the graphite, in much the same manner as CuO which also generates channels (*2*).

For the Cr_2O_3 catalyzed carbon–oxygen reaction, it was observed that the particles remained motionless while the recession rates of the distant thick edges were increased (*14*). It was suggested that Cr_2O_3 acts as a dissociation center for O_2 providing atomic oxygen which subsequently diffuses to the active sites at the pit edges where reaction occurs (*13, 14*). Marsh and O'Hair (*36*) have studied by optical microscopy the oxidation of deep edges, on the graphite basal plane, by atomic oxygen. They noted that the sides of the deep hexagonal pits, created first by oxidation with O_2 at 800°C, did not appear to recede when exposed to atomic oxygen at 200°C. There was, however, a general removal of carbon from the basal plane without any apparent widening of the hexagonal pits. Photographs of the sample after prolonged exposure to atomic oxygen showed the pits getting shallower and eventually disappearing. It was postulated that the primary mechanism of reaction consisted of chemisorbed oxides migrating on the basal plane to the edge and reacting with the uppermost layers of graphite. The recession of a few atomic layers of graphite could not be observed in an optical microscope; thus the walls of the pits appeared to be stationary. This result is supported by the results of Rellick *et al.* (*37*), who noted that the edges of various compression annealed pyrolytic graphites formed terraces after thermal oxidation, and Feates (*38*) who noted that in the radiolytic oxidation of graphite by various gases only the uppermost layer of the edge was attacked. If Cr_2O_3 did indeed act as a dissociation center for molecular oxygen, then deep edges should not have receded uniformly. On the other hand, the aforementioned mechanism of emission trapping on edges followed by direct-contact catalysis can more adequately interpret the previous results (*14*).

A final note may be made concerning the possible effects of the impurities indigenous to the graphite sample. All samples used in this study were prepared and cleaned by the method originated by Hennig (*16, 23*), i.e., repeated washing in hot HCl and HF solutions and rinsing in distilled water (*26*). This method was followed by all later workers except that some additional cleaning techniques were adopted subsequent to the acid washing step. Hennig measured the C–O_2 rates on samples further cleaned by annealing at 3100°C and separately, by electron bombardment in "high vacuum" at 2300°C, but noted that no difference was observed in the loop expansion rates (*39*). This result indicated that the impurities were not present on the freshly cleaved surfaces. A further comparison can be made on the rates of the uncatalyzed C–O_2 reaction reported by several groups using the same EDTEM technique and the same source of graphite. Turnover frequencies may be calculated from the literature data and normalized to the conditions of 0.2 atm O_2 and 650°C. Our rates were 0.6 s^{-1} (at 10 pits/μm^2) and 0.9 s^{-1} (at 1 pit/μm^2) (*28, 29*). Hennig's rate was 0.8 s^{-1} (pit density not reported but estimated to be 5 pits/μm^2) (*39*), and the rate of Feates and Robinson was, at 600°C, 0.7–0.8 s^{-1} (pit density not reported but estimated to be 3 pits/μm^2) (*25*). Clearly there is a general agreement of the data among the three groups. The sample cleaning procedure was not described in Ref. (*25*), but it was noted in other related papers by Feates *et al.* as annealing *in vacuo* at 2400°C by electron bombardment after acid washing (*38*). Using samples cleaned in the same method as that of Feates *et al.*, Evans and Thomas reported a rate of ca. 0.2 s^{-1}, normalized to the above conditions (*40*). Their samples might have very low pit densities which would yield low rates. However, their rate was still lower than that of the other groups. When impurities are present on the basal plane surface, most of them will create channels and deep pits. The results presented in this study were without channels and deep pits. Although the absence of pits and channels does not guarantee the absence of imputities, it is unlikely that these impurities, and hence the catalytic effects, would be present in the same quantities from sample to sample. Based on the above discussion, the possible effects from impurities were most likely absent in this study.

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