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Mechanism of Coke Deposition on the Surface of Molybdenite

R. T. YANG AND K. L. YANG

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

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The formation of coke is studied by SEM/TEM on the basal plane of a thin (ca. 500 Å) single-crystal film of MoS_2. From exposure to benzene at 550 and 700°C, which is exothermic in decomposition, carbon islands are formed on the face opposite to the exposure face; whereas for the endothermic decomposition of methane (at 700°C), carbon islands are formed on the exposure face. This result provides a direct evidence for the carbon diffusion mechanism for coke deposition in which a temperature gradient is the driving force for carbon diffusion. It is demonstrated that the formation and growth of thin (perhaps monolayer) carbon islands can be studied by gold decoration/TEM. A gold-decoration/TEM study of coke formation of benzene on MoS_2 show that screw dislocations are not preferred sites for carbon deposition, and that steps on the basal plane are likely the active sites for decomposition of benzene. © 1984 Academic Press, Inc.

INTRODUCTION

It has been well known since the 1940s that heterogeneous nucleation occurs preferentially at defects and steps on the solid surface, and the nuclei-decorated defects and steps can be visualized with optical microscopy (*1*). Using the transmission electron microscope (TEM), Bassett in 1958 (*2*) was able to show the presence of monotonic steps (2.8 Å height) on the cleaved surface of rock salt by gold decoration. Bassett's work was followed by the development of etch-decoration TEM technique to study the gas–graphite reactions (*3, 4*). The etchant gas is used to expand the vacancies developing monolayer pits which are visualized in TEM after gold decoration. The technique has been used fruitfully for studying gas–carbon reactions (*5*). It is also applicable to other crystals possessing layer structures. By gold decoration following etching with 10 Torr O_2 at 600°C (for a few minutes), the vacancy concentration on the basal plane of a naturally occurring MoS_2 (originating in New South Wales) was measured as 10^6 cm^{-2} (*6*). The first objective of this study is to test and demonstrate the utility of the gold decoration/electron microscopy technique in studying coke formation on surfaces of single-crystal catalysts which possess layer structures such as MoS_2.

The subject of mechanism and kinetics of coke formation from hydrocarbon vapors on catalyst surfaces has been reviewed (*7–10*). Studies on this subject have been made on polycrystalline catalysts, mostly transition metals. A generally accepted mechanism is the carbon diffusion mechanism, originally proposed for filamentous carbon formation on a polycrystalline metal (*11*). One of the remaining questions on this mechanism concerns the driving force for carbon diffusion. The more specific objective of this study is, by using a thin film of single crystal, to test the carbon diffusion mechanism and to provide an answer to the question of driving force for the mechanism. Results on coke formation from an exothermic decomposition (of benzene, $\Delta H_f = -61.9$ kJ/mole) and an endothermic decomposition (of methane, $\Delta H_f = 74.9$ kJ/mol) will be presented.

EXPERIMENTAL

Carbon was deposited on the basal, or {0001} plane of natural molybdenite (MoS_2)

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crystal (originating in Froland, Arendal, Norway), from benzene at 550 and 700°C and from methane at 700°C. (Homogeneous decomposition of benzene is not important at below ca. 750°C, methane at still higher temperatures.) Thin, flat sections (cleaved to about 500 Å) of the sizes of approximately 2 mm of MoS_2 were supported on the flat surface of a sapphire plate. In studies of gas–graphite reaction using the same arrangement, etch pits were found only on the face exposed to the gases, not on the face lying on the sapphire plate (*5*). Prior to exposure to hydrocarbon gases, the samples were "degassed" at 650°C for ca. 10 h in flowing argon and subsequently treated with H_2S at 350°C for 10 min. The H_2S treatment was used to ensure that the surface was sulfided in the event that sulfur was detached from the surface as oxy-sulfur species (with chemisorbed oxygen) in the "degassing" step. The temperature was rapidly raised and exposure to a hydrocarbon followed. In experiments with benzene, the samples were exposed to 90 Torr benzene (carried in N_2) for a desired period of time. The N_2 carrier was of oxygen-free grade (<0.5 ppm O_2, Linde) and was further passed through copper turnings kept at 550°C to remove the residual oxygen. Gold decoration was done in a vacuum coater by depositing gold equivalent to a monolayer coverage on the MoS_2 surface. The sample was kept at 250°C to facilitate migration and nucleation of gold atoms. The decorated samples were then examined in a TEM. For experiments with methane, the samples were exposed to 0.6 atm CH_4 at 700°C for 3 h. The detailed procedures for sample cleavage, cleaning, gold-decoration, etc. were the same as those used in our studies of the gas–carbon reactions (*5*).

RESULTS AND DISCUSSION

The first objective of using a thin film to study coke formation is to be able to detect and measure minute amounts of carbon formed on the surface, such as small monolayer islands, by gold decoration/TEM. Using cleaved single crystals with layer structures provides the additional advantage for studying well-defined surfaces. Knowledge on coke formation in the initial period, or, the generally known "induction period," is crucially important in our understanding of the mechanism of coke formation.

On the MoS_2 film/hydrocarbon system, the first question addressed in this study is on which side(s) of the MoS_2 crystal is carbon deposited?

Coke Formed from Benzene

Triangular islands of carbon are seen with both TEM and SEM. Most interestingly, the islands are found only on the MoS_2 face which is opposite to the face exposed to benzene. No carbon islands are found on the exposed face. Figure 1 is a TEM picture showing the carbon islands deposited with apparently random orientations. Figure 2 shows the islands, in SEM from a tilted angle, formed on the hidden face (basal plane) of the MoS_2 crystal. Thin carbon islands, as revealed by gold decoration, are also found only on the hidden face (micrographs to be shown later).

Coke Formed from Methane

The islands formed from CH_4 on MoS_2 as shown in TEM (Fig. 3) and SEM (Fig. 4) are not faceted. More important, examination of the coked sample in SEM reveals that the coke islands are formed on the face exposed to CH_4, contrary to the result with benzene. The height of the islands is approximately 0.5 μm as estimated from the SEM picture where the sample is tilted at an angle of 71°.

The Diffusion Mechanism and the Driving Force for Diffusion

The carbon diffusion mechanism is a generally accepted mechanism originally proposed by Baker and co-workers (*11*) to account for the formation of carbon filaments on polycrystalline metal surfaces and supported metal catalysts. According to the

FIG. 1. TEM micrograph of carbon deposited on the basal plane of MoS_2 crystal from exposure to 90 Torr benzene at 700°C for 1 h.

theory, the hydrocarbon decomposes on the front-exposed surface of the metal particle or grain to release hydrogen and carbon, which dissolves in the metal. The dissolved carbon diffuses through the particle and is precipitated on the rear face to form

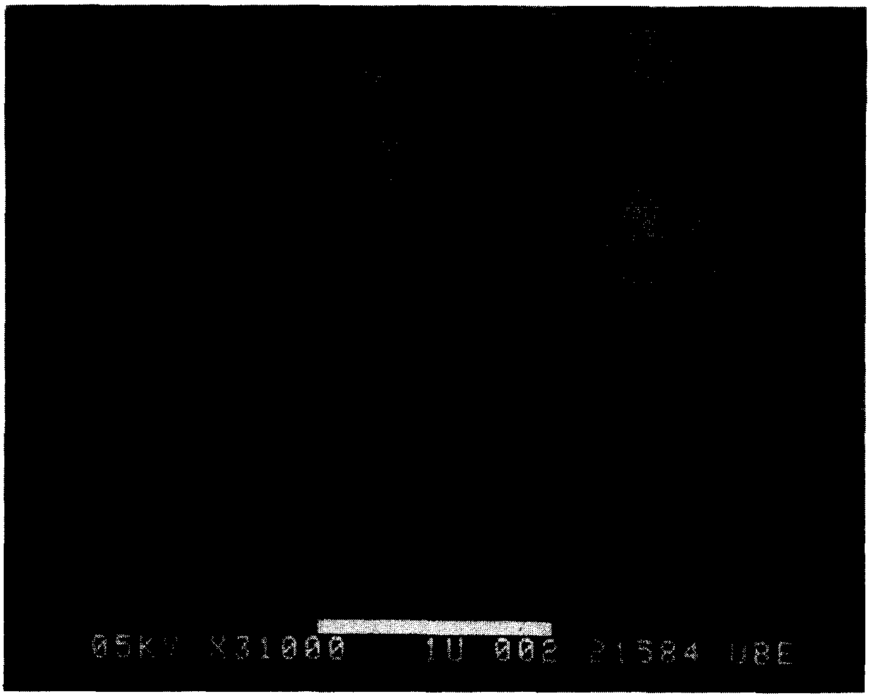

FIG. 2. SEM micrograph of carbon islands formed on the basal plane of MoS_2 after the opposite face of the crystal is exposed to 90 Torr benzene at 550°C for 2 h.

the body of the filament. In a polycrystalline metal the filament growth is initiated by loosening the grain boundaries where carbon is precipitated and the detachment of the metal particle at the grain boundaries. The diameter of the carbon filament is thus the same as that of the particle which is usually bound at the tip of the filament. An important observed fact is that the diameters of the filaments are generally small, e.g., below 0.1–0.2 μm (which is near the thickness of the MoS_2 film used in this study). Although the diffusion mechanism is accepted, the nature of the driving force for diffusion has been under debate. Baker suggested that the heat of decomposition (exothermic) on the front-exposed face is removed by the endothermic process of deposition of carbon from the metal on the rear face of the particle. Using the C_2H_2/Ni system as an example, the heat release on the exposed face is equal to $-\Delta H_f$ for C_2H_2 + ΔH_{soln} for C in Ni, or -223.6 and -40.5 kJ/mol, and the heat absorbed on the rear face is $+40.5$ kJ/mol (*11*). The difference between the source and the sink is transferred to the surroundings by radiation and convection. A temperature gradient (estimated as near 30°C) is maintained across the metal particle. Rostrup-Nielsen and Trimm suggested, based on the argument that endothermic coking (such as from CH_4) also forms filaments (which has been questioned by Baker regarding the impurity hydrocarbons contained in CH_4), that concentration gradient is the driving force for carbon diffusion (*12*). The concentration gradient is due to the difference between the solubilities of carbon in metal from the hydrocarbon and from graphite. Because such a gradient, if indeed exists, is likely to be small, they further proposed that screw dislocations on the rear face serve as preferred sites, and hence a sink, for carbon deposition. (An immediate question which can be raised concerns the role of the equal number of dislocations on the front and side faces.)

FIG. 3. TEM micrograph of carbon deposited on the basal plane of MoS_2 crystal from exposure to 0.6 atm CH_4 at 700°C for 3 h.

FIG. 4. SEM micrograph of carbon islands formed on the basal plane of MoS_2 after exposure of the crystal to 0.6 atm CH_4 at 700°C for 3 h. Carbon is deposited on the exposure face.

The experiments using thin films of single-crystal MoS_2 (ca. 500 Å thickness) provide an ideal test for the carbon diffusion mechanism. Our TEM results discussed in the foregoing show that coke formed from CH_4, which is endothermic, is deposited on the front, exposed face whereas it is formed on the face opposite to that exposed to benzene, which is an exothermic reaction. The results provide a direct evidence for the carbon diffusion mechanism and, more important, show that temperature gradient is the driving force for carbon diffusion.

For the benzene/MoS_2 system, surface diffusion of carbon around the crystal edges is unlikely because (1) the carbon islands are randomly distributed on the rear face and (2) the MoS_2 crystal may be viewed as a two-dimensional crystal due to the high area/thickness ratio. The mechanism of benzene decomposition on the front face is not clear, which forms carbon and either H_2 (*13*) or CH_4 (*14*).

Data on the solubility of carbon in MoS_2 are not available. However, there are at least six known carbide phases in the Mo–C system (*15*) and some of the phases can be readily formed by reacting Mo with hydrocarbons such as CH_4 and naphthalene at mild temperatures (300–700°C) (*16*). This information, in the absence of any data on the MoS_2–C system, could serve as a support for the dissolution/diffusion mechanism. The carbide phases could also play a role in the decomposition of benzene (*17*, *18*).

Gold Decoration/TEM

Exposure of MoS_2 to benzene (90 Torr) at 550°C for short periods of time yields thin carbon islands, some of which are barely visible in the TEM (which is equivalent to a graphite layer slightly thicker than 1000 Å (*3*, *5*)). Gold decoration on the face previously exposed to benzene results in random gold nuclei (Fig. 5). The carbon island

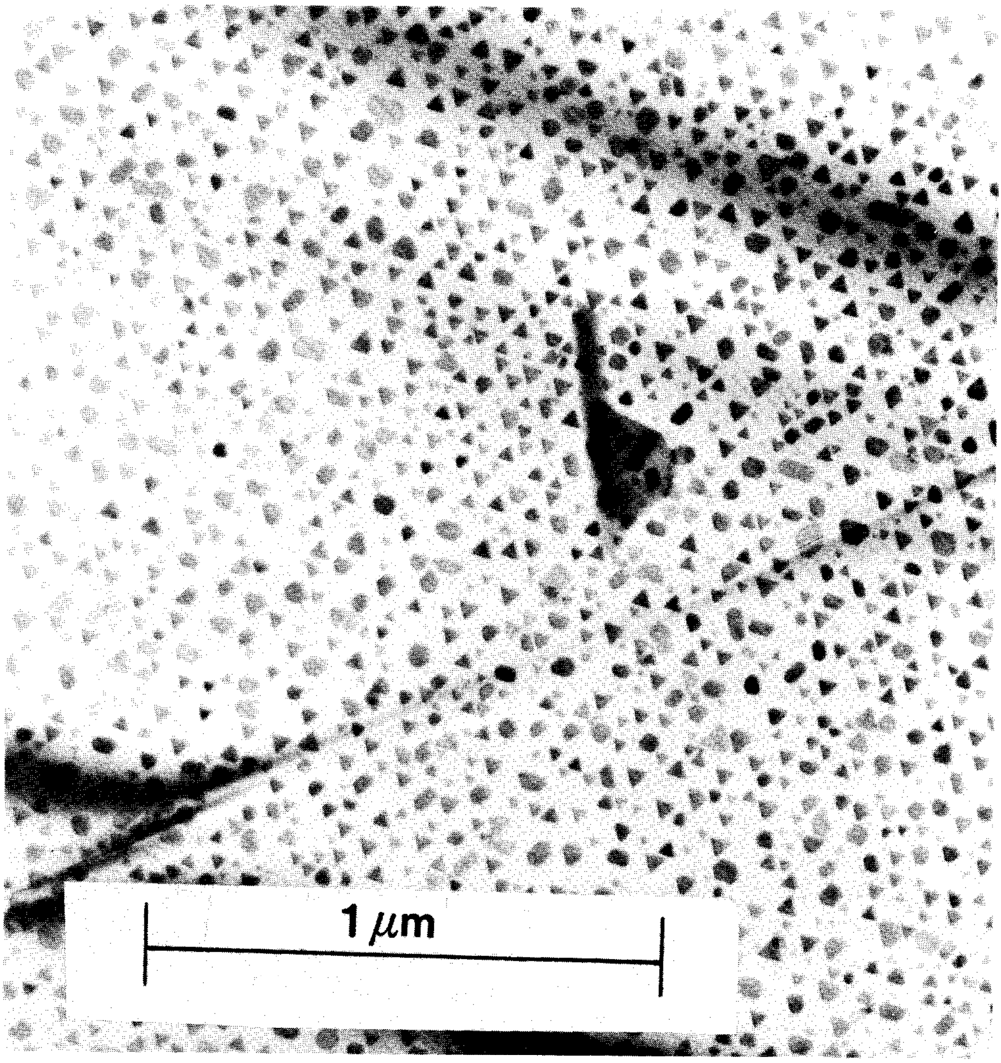

FIG. 5. TEM micrograph of gold-decorated MoS_2 film. Gold vapor is deposited on the same face of the film which has been previously exposed to 90 Torr benzene at 550°C for 25 min. Note the carbon island and gold nuclei are clearly on opposite faces.

shown in Fig. 5 is not decorated by gold on its edges, and it is clear that the island is on the opposite face of the MoS_2 crystal. Decoration on the face opposite to benzene exposure show gold nuclei forming triangles.

In order to increase the density of carbon islands, the MoS_2 crystal is first etched by O_2 (0.1 atm O_2 at 600°C for 6 min) prior to benzene exposure. The etching increases the number of steps which are thought to be the active sites for coke formation. After O_2 etch and benzene exposure (90 Torr, 550°C for 20 min), both on the same face, gold is decorated on the opposite face. TEM graph of the decorated MoS_2 are shown in Figs. 6 and 7. The decorated triangles are apparently thin carbon islands (possibly monolayer thick), which are generally formed in lines (Fig. 6). This observation indicates that the steps on the opposite face are the active sites for carbon formation from benzene. Screw dislocations are also decorated

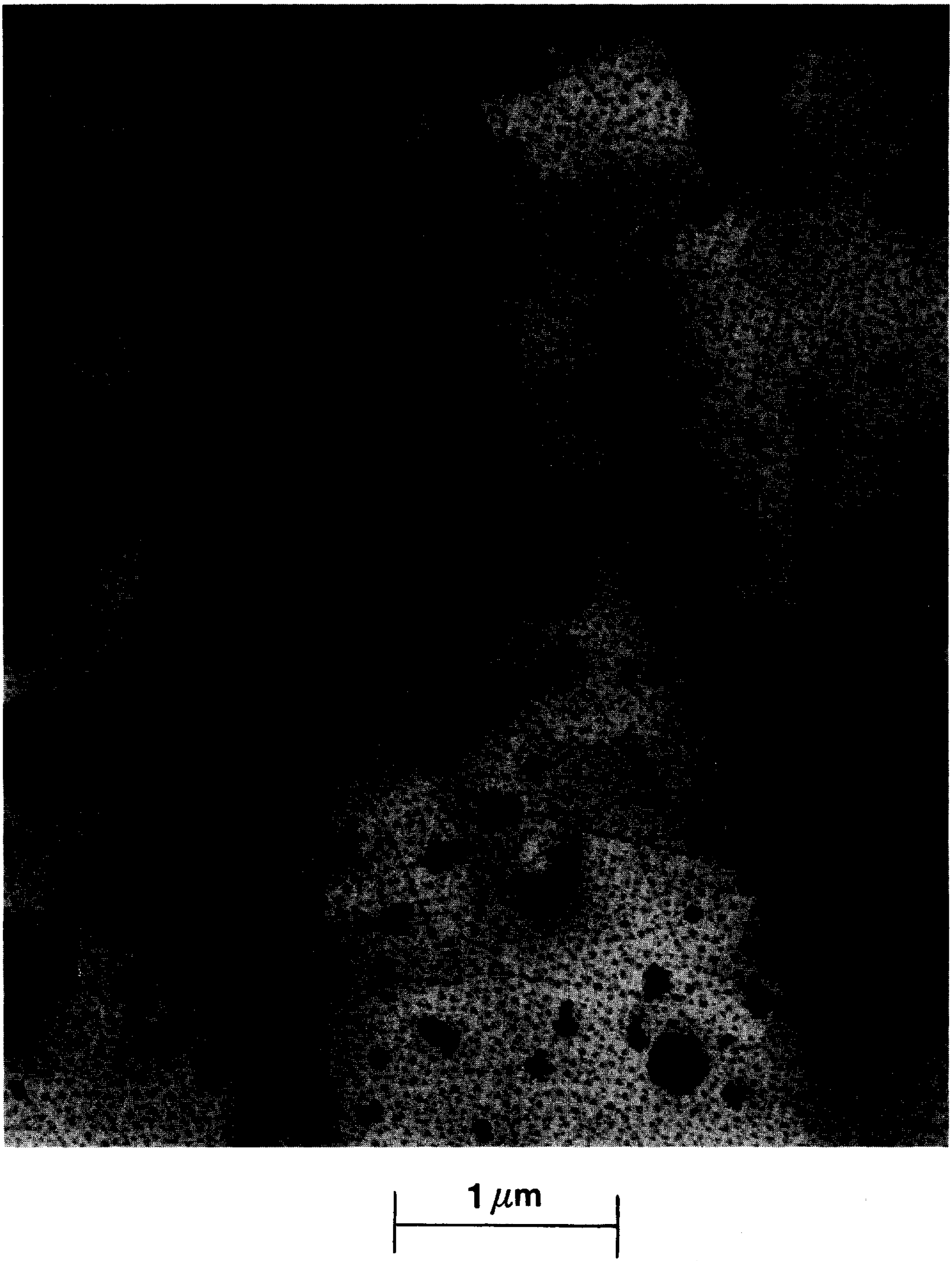

FIG. 6. TEM of MoS_2 sample after the following treatments: etched with 0.1 atm O_2 at 600°C for 6 min, exposure of the etched face with 90 torr benzene at 550°C for 20 min, and gold decoration on the face opposite to etching and benzene exposure. All decorated carbon island appear in lines.

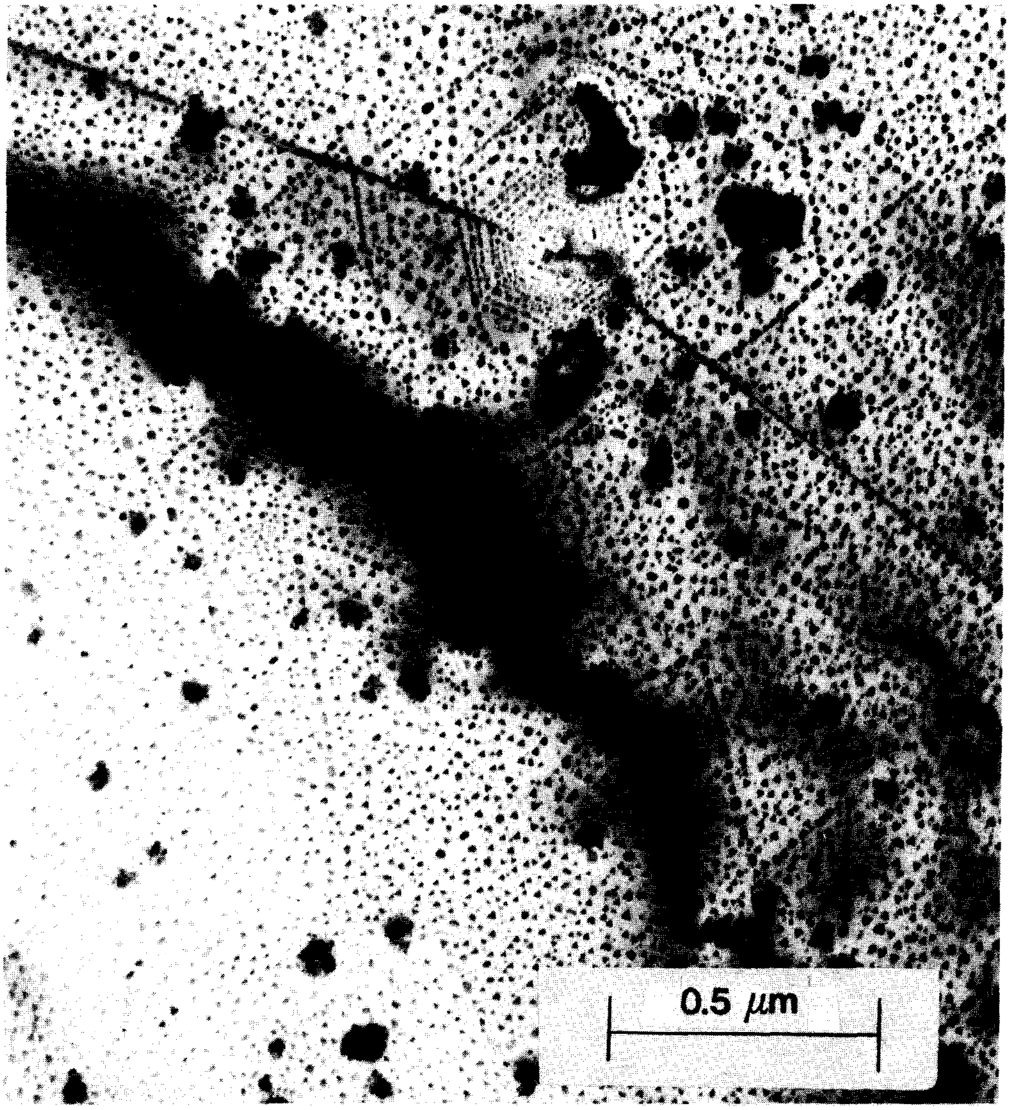

FIG. 7. Same as in Fig. 6. A gold-decorated screw dislocation is shown.

and seen in the TEM. The density of screw dislocation in the MoS_2 crystal is apparently higher than that of vacancies. The density of screw dislocation in the samples examined in this study is approximately 5×10^6 cm^{-2}. An example of the decorated screw dislocation is shown on Fig. 7. An effort has been made to locate carbon islands formed on the screw dislocations, but they are generally free of carbon. This result concludes that screw dislocations are not the preferred sites for coke deposition, as suggested previously (*7, 12*).

Electron Diffraction Patterns of Coke Samples

The coked samples have been further subjected to electron diffraction analysis, in order to obtain an understanding of the nature of the coke. Figure 8a is the selected-area diffraction pattern of the bare surface of the sample coked by 90 Torr benzene at

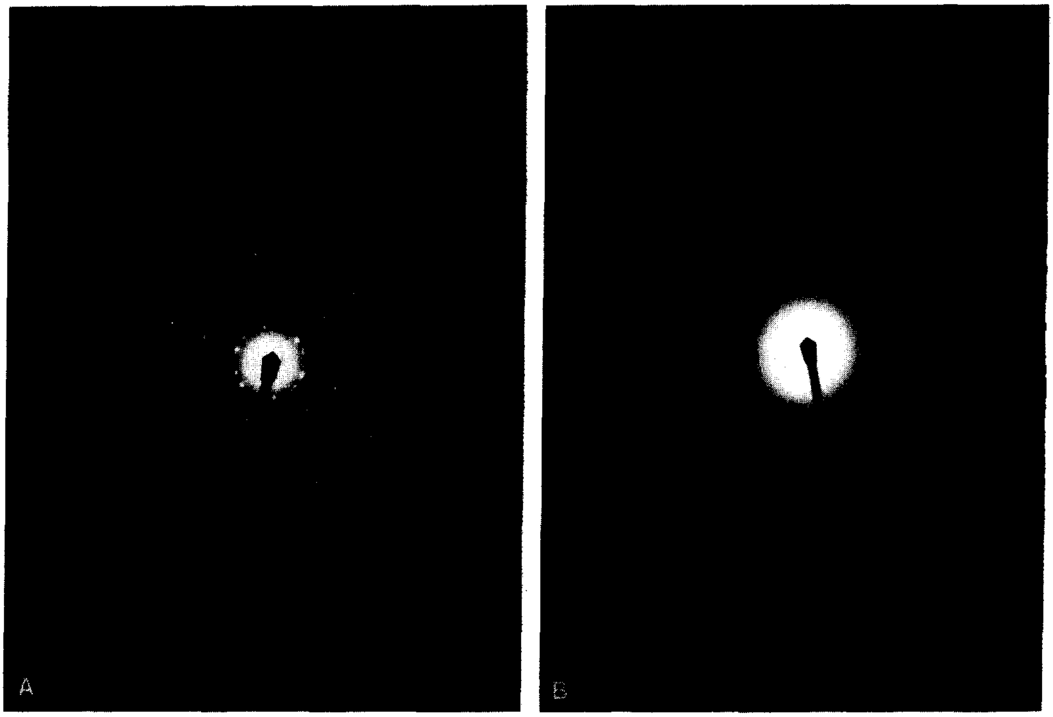

FIG. 8. Electron diffraction patterns of the coked MoS_2 sample, the TEM of the same sample is shown in Fig. 1. (A) Pattern of the bare MoS_2 surface. (B) Pattern of the coke islands, which is identical to that of single-crystal graphite.

700°C for 1 h. Figure 8b is the pattern for the triangular islands on the same sample. These patterns correspond to, respectively, single crystals of MoS_2 and graphite. The electron diffraction pattern of the thin triangular islands on the sample coked with CH_4 at 700°C, the TEM of which is shown in Fig. 3, has also been taken. This pattern, again, shows that the thin islands are single-crystal graphite. Diffraction patterns of the samples coked at 550°C have not been taken. The electron diffraction analysis shows unequivocally that the coke shown in this study is indeed carbon.

CONCLUSIONS

Using the technique of gold decoration and TEM/SEM, the study of coke formation from benzene and methane on the basal plane of thin (ca. 500 Å) MoS_2 single crystals show

1. For coke deposition from benzene, which is exothermic, faceted (triangular-shaped) carbon islands are formed on the face opposite to exposure to benzene; whereas for CH_4, unfaceted carbon islands are formed on the face of exposure. This result provides a direct evidence for the carbon diffusion mechanism and that the diffusion is driven by a temperature gradient.
2. The technique of gold decoration/TEM can be used to detect the formation and growth of thin (perhaps monolayer) carbon islands.
3. Screw dislocations are not preferred sites for carbon deposition.
4. Steps on the basal plane are likely the active sites for benzene decomposition and carbon formation.

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