JOURNAL OF CATALYSIS **140**, 287–301 (1993)

Interaction of Hydrogen with Metal Sulfide Catalysts—Direct Observation of Spillover

N. M. RODRIGUEZ AND R. T. K. BAKER[1]

Department of Chemical Engineering, Auburn University, Auburn, Alabama 36849

Received May 21, 1992; revised July 20, 1992

A combination of controlled-atmosphere electron microscopy and *in-situ* electron diffraction techniques have been used to study the manner by which certain metal sulfides interact with 0.2 Torr hydrogen. In these experiments single crystal graphite was used as a probe material since its reactivity in both molecular and atomic hydrogen is well characterized. When the metal sulfide was in direct contact or physically separated from the graphite probe, pitting of the basal plane regions was observed even at room temperature. This unusual behavior is believed to result from the action of atomic hydrogen which is produced via reversible dissociation of molecular hydrogen on the metal sulfide particles. These species are extremely reactive towards the π-electrons present on the graphite basal planes and this action leads to the creation of pits. At the low pressures used in this work, it is clear that the atomic species can migrate not only by surface diffusion processes (spillover) but also by transport through the gas phase. © 1993 Academic Press, Inc.

INTRODUCTION

Transition metal sulfides are used extensively as hydrotreating catalysts with the most important reaction in this category being hydrodesulfurization (HDS), and there are a number of excellent reviews on this subject (*1–4*). In such systems the precise manner by which hydrogen interacts with the sulfide catalyst is a key factor to the understanding of the mechanism. The reaction of metal sulfide catalysts with hydrogen is a complex process and is dependent to a large degree on the structural features of the system. Most fundamental experimental and theoretical studies have focused attention on molybdenum disulfide, which possesses a layered lattice structure in which Mo^{4+} cations are located at the centers of triangular prisms. The MoS_2 layers are bonded to one another by van der Waals interactions through the S^{2-} anions. In this type of structure atoms on the basal plane differ from those located at edges and consequently give rise to differences in their mode of interaction. It is generally believed that the edge sites are responsible for the activity of this type of catalyst, with the basal plane being relatively inert (*5*).

Stevens and Edmonds (*6*) investigated the interaction of hydrogen on various MoS_2 samples and found that adsorption on the edge sites commenced at about 155°C and reached a maximum at 225°C. In contrast, temperatures of 205°C were required to induce adsorption of hydrogen on the basal plane regions and this process occurred to a substantially lower degree. Edge site adsorption was shown to be completely reversible in nature with no products been detected during the desorption step. Wright *et al.* (*7*) studied the interaction of hydrogen with alumina-supported molybdenum disulfide catalysts using a combination of hydrogen adsorption and inelastic neutron scattering techniques. They found that the uptake of hydrogen was several times higher than that which was expected from nitrogen adsorption experiments. In order to account for this unusual behavior, they suggested

---

[1] Authors' present address: Materials Research Laboratory, Department of Materials, The Pennsylvania State University, University Park, PA 16802.

0021-9517/93 $5.00

that the adsorption of extra hydrogen could arise from intercalation into the layered structure of the sulfide particles or alternatively as a result of hydrogen "spillover" onto the alumina support. Furthermore, they concluded that hydrogen reacted with the supported catalyst to form S–H groups on the MoS_2 crystallites and was also present on the alumina. Significantly, no evidence for the presence of SH_2 groups or molecular hydrogen was found on the surfaces of the MoS_2. Similar conclusions have recently been reported by Polz *et al.* (*8*) from their work using both polycrystalline MoS_2 and alumina supported sulfided Mo catalysts. They suggested that the high H/Mo ratios obtained for the alumina supported catalysts (~4) were the result of a combination of higher surface areas and hydrogen "spillover." Raman spectroscopy studies indicated two possible mechanisms for hydrogen dissociation, heterolytic dissociation on Mo–S pairs and homolytic dissociation on disulfide $(S–S)^{2-}$ edge groups, however, it was not clear which particular sites were responsible for the activation and eventual dissociation of hydrogen molecules (*9*).

Baker *et al.* (*10*) used *in-situ* electron microscopy techniques to study the reactivity of molybdenum disulfide in various gaseous environments, including hydrogen. They reported that the reduction of single crystal MoS_2 in hydrogen was a relatively sluggish process and that attack appeared to be confined to the edge regions. Complementary *in-situ* electron diffraction analysis showed that at 365°C loss of sulfur in the form of H_2S resulted in the formation of Mo_2S_3 and as the temperature was increased to 675°C there was evidence for the formation of metallic Mo.

In the current investigation we have attempted to gain a clearer understanding of the manner by which hydrogen interacts with various metal sulfides, including MoS_2, FeS_2, and FeS as a function of temperature by using controlled-atmosphere electron microscopy techniques to investigate a model system consisting of single crystal graphite, a well characterized material for which reactivity with hydrogen in the presence of metal additives has been extensively studied (*11*).

EXPERIMENTAL PROCEDURE

The experiments reported here were carried out in a modified JEOL 200CX TEM electron microscope. This instrument is equipped with a custom designed environmental cell, which accommodates a heating stage. Specimens can be heated up to a temperature of 1000°C while at the same time being exposed to a gas environment at pressures up to 3.0 Torr. The resolution of this instrument when used in conjunction with a high sensitivity closed-circuit television system is of the order of 0.4 nm (*12*). In addition to being able to directly follow changes in the appearance of a specimen as it is undergoing reaction, it is also possible to use the microscope in the diffraction mode and obtain information about the chemical state of the specimen at any stage of the experiment.

Transmission specimens of single crystal graphite and molybdenum disulfide were prepared by a standard cleaving procedure (*13*). Metal sulfide powders, ultrasonically dispersed in iso-butanol, were introduced onto thin sections of single crystal graphite and mounted onto microscope grids. With this procedure it is possible to obtain a dispersion of small particles about 5 nm in size. Metals were deposited onto the graphite substrates by evaporation of spectrographically pure iron wire from a tungsten filament and by passing a high current through a molybdenum filament at a residual pressure of 10^{-6} Torr. The conditions were selected so as to produce a film of metal at least one atom on average thickness.

In this investigation two types of specimen arrangements were utilized, which are shown schematically in Fig. 1. In layout (a), the catalyst particles (metal or metal sulfide) were placed in direct contact with the graphite specimen, and the observations made were limited to areas in the vicinity of the

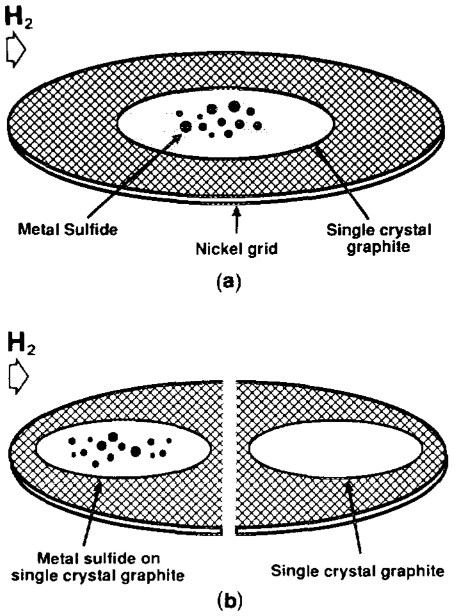

FIG. 1. Schematic representation of specimen arrangements: (a) metal sulfide catalyst and single crystal graphite probe in direct contact; (b) metal sulfide and graphite probe physically separated.

catalyst particles. For the second design (b), a microscope grid was cut in half and one section contained a pristine transmission graphite specimen and on the other, the catalyst mounted in the same manner as shown in (a) or in the form of a crystal of molybdenum disulfide. In this arrangement the catalyst and graphite probe reactant were physically separated. It was essential that when this type of specimen was placed into the environmental cell the reactant gas stream came into contact with the catalyst prior to passing over the clean graphite, the component under observation. In a complementary series of reactions pristine samples of graphite mounted on nickel grids were treated under the same reaction conditions in order to establish the effect of both the electron beam and the presence of the metal on the reaction.

Single crystal molybdenum disulfide and graphite originated from Froland, Norway, and Ticonderoga, New York, respectively. Iron sulfides and molybdenum sulfide powders (99.9% purity) were purchased from Aldrich Chemical Co. Inc; iron, and molybdenum wires (0.127 mm diam.) both 99.999% purity were purchased from Alpha Products. The reactant gas, hydrogen (99.999% purity), was obtained from Alphagaz and used without further purification.

RESULTS

(a) Metal Sulfides/Graphite–Hydrogen

When graphite specimens containing particulates of either molybdenum disulfide or the iron sulfides (FeS_2 or FeS) were exposed to 0.2 Torr hydrogen a very unusual pattern of behavior was observed. Immediately following the introduction of the gas attack of the basal plane regions of the graphite support took place at room temperature. This action initially took the form of the creation of very tiny pits which became visible when their width had expanded to approximately 1.2 nm and their depths reached a level sufficient to allow a contrast difference to be observed in the transmission image between the pit and the surrounding unattacked graphite. In some cases the presence of very shallow pits, which would not be observed by conventional transmission electron microscopy, was revealed due to the formation of relatively dense residues produced in the reaction which accumulated at the pit boundaries.

It was evident that in the early stages of the reaction the pits tended to be generated in clusters which were aligned in definite directions with respect to the graphite substrate. Examination of numerous areas showed that the hexagonal arrangement was predominant. On continued reaction at the same temperature the pits increased in size and in a given group gradually merged with each other to form a single larger entity up to 10 nm in width. Examination of these more highly developed pits showed that they tended to acquire a hexagonal outline and at this stage generally contained an internal region of unattacked carbon. The ap-

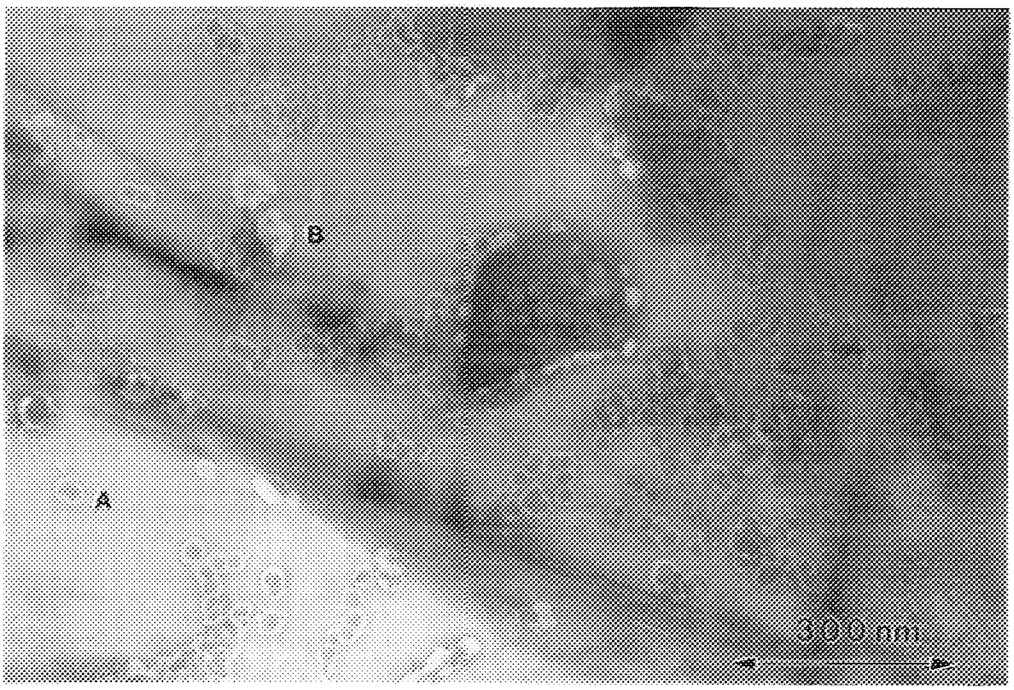

FIG. 2. Transmission electron micrograph of a molybdenum disulfide/graphite specimen which has been reacted in 0.2 Torr hydrogen at room temperature. The locations (A) and (B) indicate the appearance of pits in the early and more developed stages, respectively.

pearance of pits produced on graphite in the presence of an molybdenum disulfide catalyst following reaction in hydrogen for 5 min is shown in the transmission electron micrograph, Fig. 2. Inspection of this micrograph shows the development of the pits from a hexagonal outline (A) to the state (B) where expansion and removal of the inner region has occurred, however, in this region it is significant that no metal sulfide catalyst particles are visible.

A more mechanistic approach to the understanding of the mode by which the initial and more developed pits are formed on the basal plane of graphite is shown in the schematic rendition, Fig. 3. The orientation of the so-called armchair face $\{11\bar{2}l\}$ and zigzag face $\{10\bar{1}l\}$ are also indicated in this diagram. Although the regions of graphite in direct contact with metal sulfide particles were readily attacked, it was significant to find that pits were also produced at locations remote from the catalyst. Such sites were generally in the vicinity of surface imperfections such as vacancies, emergent dislocations, steps and along twin bands.

The expansion of pits produced on FeS/graphite specimen during exposure to hydrogen at room temperature is shown in the sequence of stills taken from the TV monitor, Fig. 4. The time period between Figs. 4A and 4D is 6 min. From frame-by-frame analysis of several sequences, it has been possible to obtain a measure of the linear increase in pit width as a function of time. A typical example of the data obtained from this operation is shown in Fig. 5, and from the slope of the line a value of 0.015 nm/sec has been estimated for the rate of edge recession at room temperature.

A feature which must always be taken into consideration with experiments carried out within the electron microscope is whether the electron beam exerts any effect

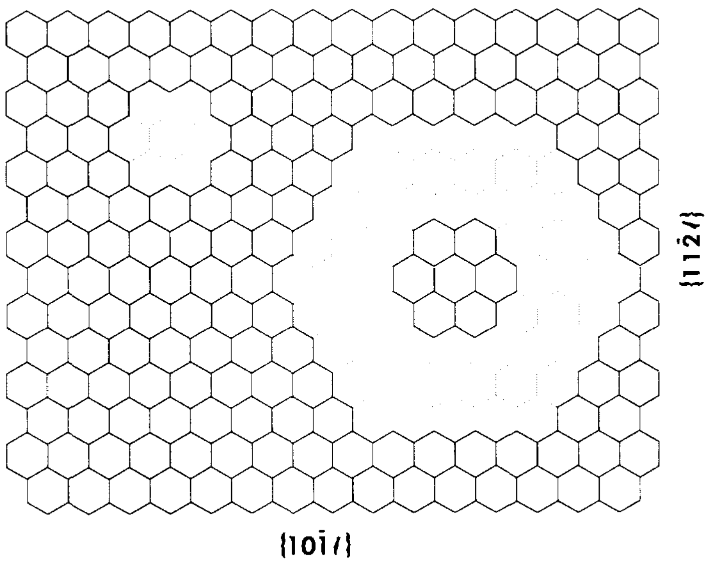

FIG. 3. Schematic representation of the basal plane of graphite showing the C–C bond cleavage processes necessary to form initial and more developed pits. Also indicated in the diagram are the Miller indices of the zig-zag {$10\bar{1}l$}, and the armchair {$11\bar{2}l$} faces.

on either the gas or the solid under investigation. Concern that this problem was being encountered in the current work was dispelled by performing "blank experiments" in which specimens were reacted in hydrogen with the beam turned off for periods of up to 2 hr. When such specimens were eventually examined it was clear that there have been extensive reaction prior to exposure to the beam. In contrast, when clean graphite specimens supported on nickel grids were treated under the same conditions no change in appearance of the surface was observed, indicating that the interactions of hydrogen with either the tungsten filament or nickel grid were not exerting any influence on the reaction. As mentioned above, when graphite-supported metal sulfides were exposed to the electron beam for prolonged periods in the presence of hydrogen, a carbonaceous residue was observed to form on the surface and tended to accumulate at edge and steps sites including the walls of pits. Eventually this deposit became so heavy that many surface features were obscured and it was apparent that the gasification reaction was being inhibited. In contrast, this detrimental effect was not so pronounced in "blank experiments" carried out over the same time periods. Furthermore, when various metal/graphite specimens were reacted under the same conditions under continuous electron beam exposure then no deposition of material was observed.

As the temperature was increased to 100°C it was evident that attack became more random in nature so that the entire graphite surface gradually acquired a textured appearance. It was also apparent that pits which had been produced at lower temperatures increased in depth and tended to become progressively more circular in shape. At this stage of the reaction many pits had expanded reaching sizes of up to 4.0 μm in diameter, and frequently merged with adjacent ones with a consequence that there was wide spread removal of entire layers from the graphite surface.

The intensity of the reaction increased significantly as the temperature was gradually raised to 200°C. Unfortunately, the in-

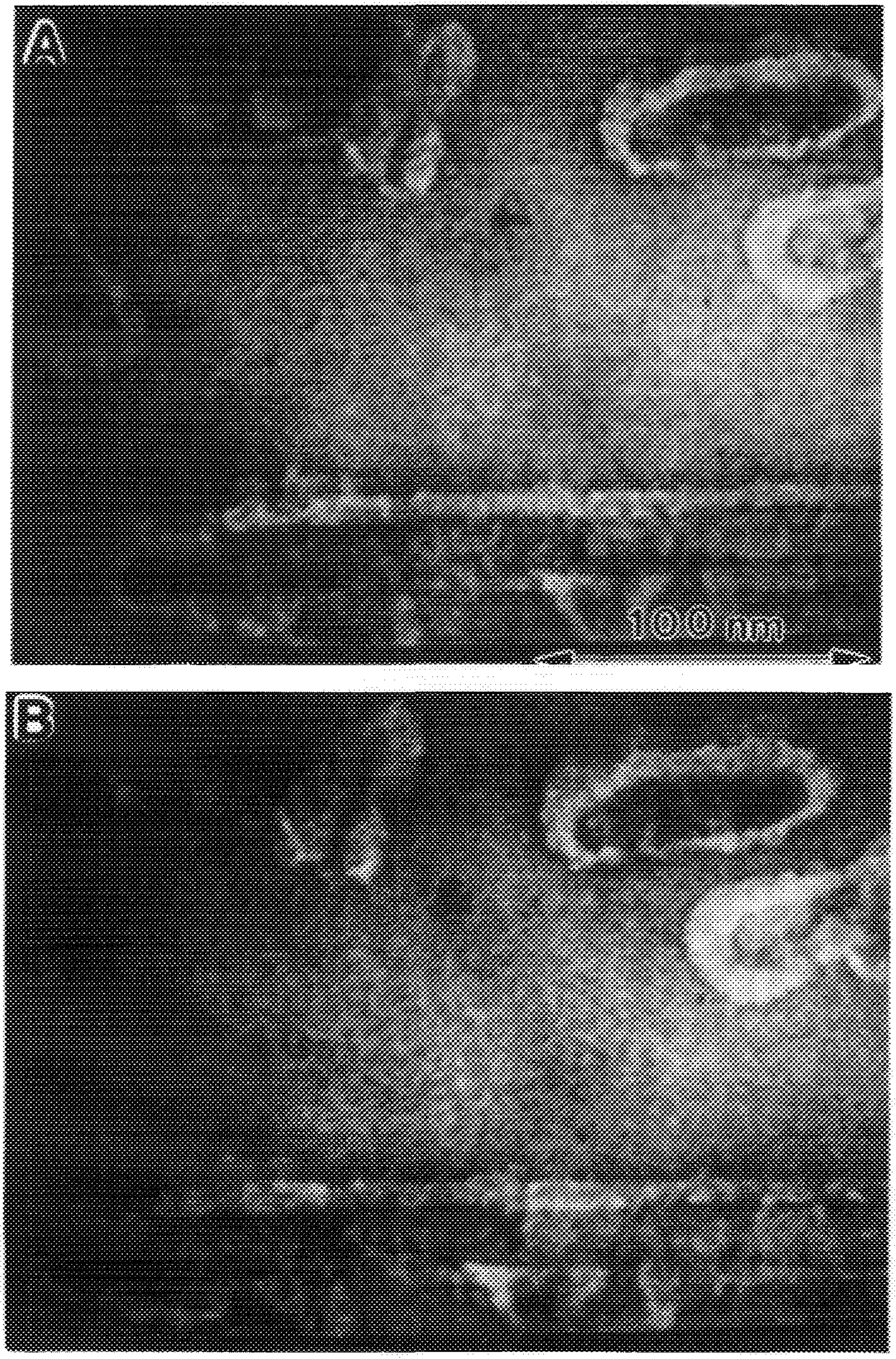

FIG. 4. A sequence taken from the television monitor over a period of 6 min showing the expansion of pits produced during the interaction of 0.2 Torr hydrogen with an FeS/graphite specimen at room temperature (see text).

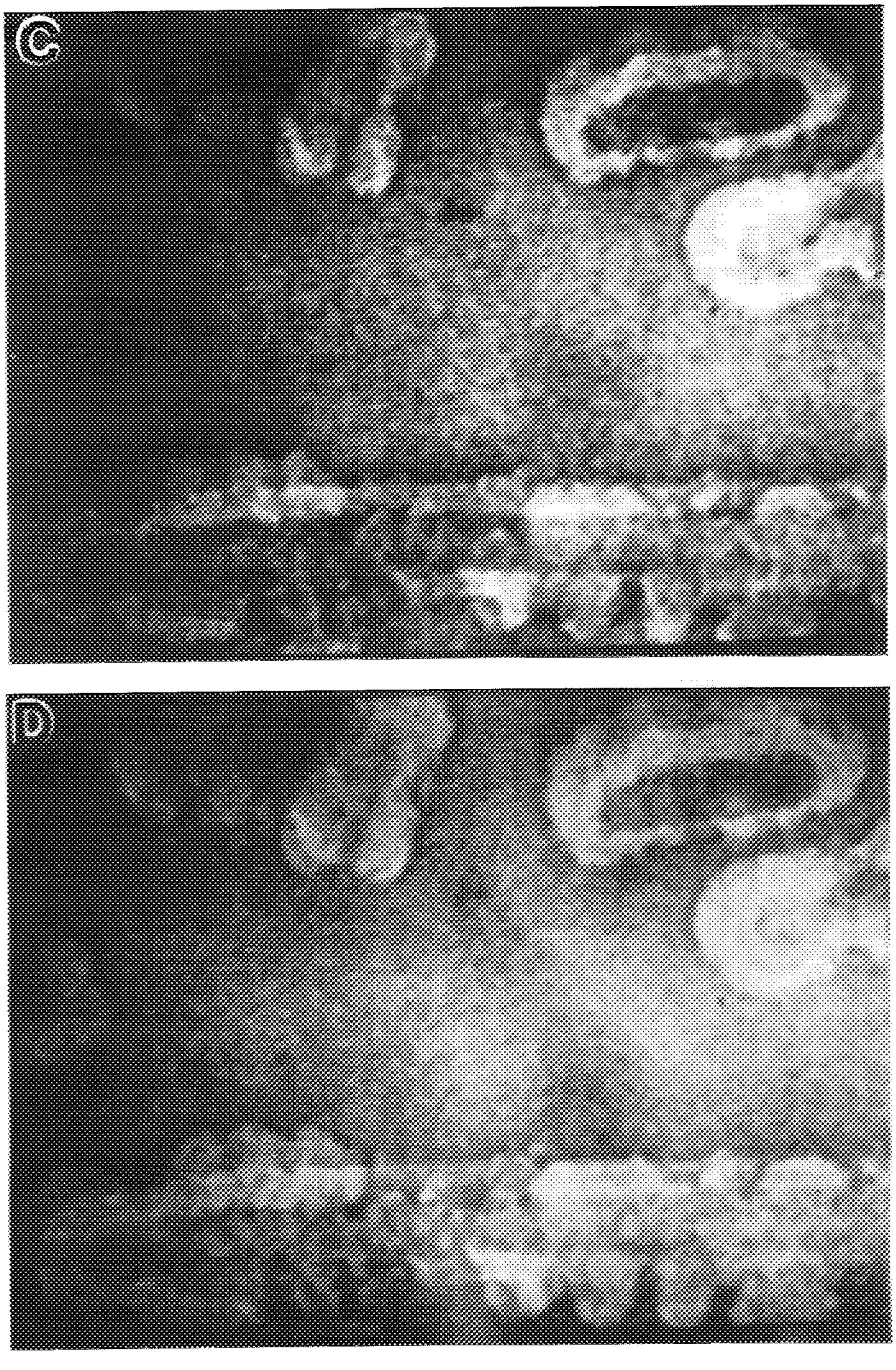

FIG. 4—*Continued*

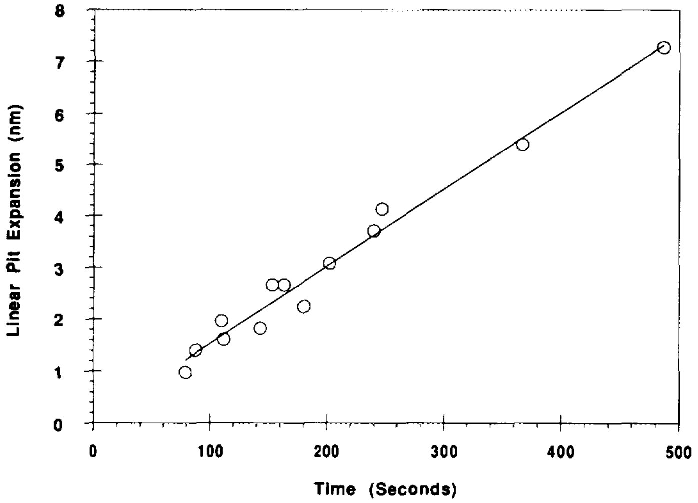

FIG. 5. A plot of the linear expansion of pits created in graphite from the interaction of FeS with 0.2 Torr hydrogen as a function of time at room temperature.

discriminate mode of attack made it impossible to identify any dynamic events that could be followed for the purposes of estimating rates of graphite hydrogenation. Moreover, the gradual deterioration in quality in the transmission image due to collection of deposit on the specimen made it difficult to resolve many surface features. In studies where the temperature was held at 350°C for extended periods of time the attack became so extensive that specimens lost their integrity and experiments were normally terminated.

On the other hand, when specimens which had been allowed to react in hydrogen at room temperature for periods of up to 2 hr were subsequently heated in a continuous fashion to about 500°C an entirely different pattern of behavior was observed. Under these conditions, the expansion of pits was arrested and the surface underwent a cleansing operation as the carbonaceous residue was removed as a result of volatilization and/or gasification. If, at this stage, the temperature was lowered to room temperature, then restoration of pitting activity could be achieved. On continued heating to above 500°C, the sulfide particles were observed to exhibit a change in morphological characteristics from faceted structures to a more globular geometry. This transformation, which occurred at about 725°C with the iron sulfides and at 775°C for molybdenum disulfide, was most clearly evident with particles located at edge regions which appeared to be quite fluid and tended to wet the graphite. This behavior was a prelude to the restoration of catalytic activity, seen as the propagation of channels by these particles when the temperature was increased by a further 100°C. An example of the channeling action is shown in the electron micrograph, Fig. 6, which was taken of a molybdenum disulfide/graphite specimen undergoing reaction in hydrogen at 900°C.

In an attempt to determine whether the catalytic action could be sustained at even greater distances from the sulfide particles, another set of experiments was carried out using a different specimen design. This involved complete physical separation of the supported metal sulfide and the graphite probe component. When this combination was treated in 0.2 Torr hydrogen then attack of the unadulterated graphite surface was once again observed at room temperaure. In

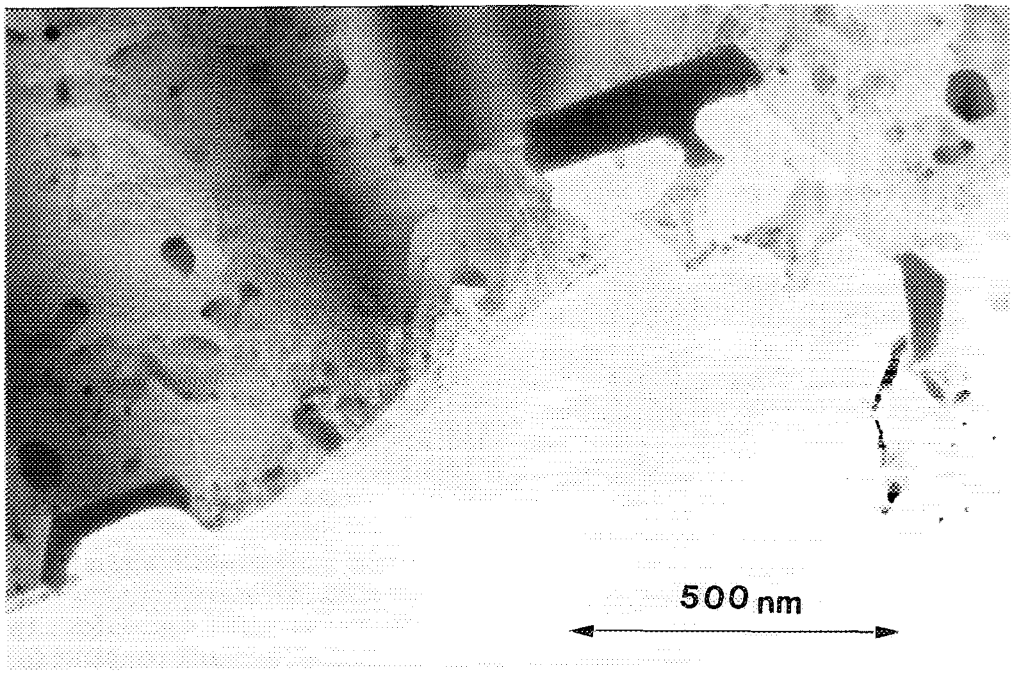

FIG. 6. Transmission electron micrograph showing the formation of channels produced across the basal plane surfaces of graphite at 900°C from a specimen on which molybdenum disulfide was initially present.

these systems, however, there was a modulation in the severity of the reaction compared to that where the catalyst and graphite were in intimate contact. It was significant to find that the incidence of pit formation showed a steady decline as one scanned across the graphite surface in the opposite direction to that where the sulfide catalyst particles were located.

(*b*) *Metal/Graphite–Hydrogen*

This series of experiments was conducted in order to provide a comparison to the events observed with the metal sulfide/graphite–hydrogen systems at high temperatures, where the catalytic action might be attributable to the presence of the respective metals. When iron/graphite and molybdenum/graphite specimens were heated in 0.2 Torr hydrogen they exhibited similar patterns of behavior. Nucleation of discrete metal particles ~2.0 nm in diameter was achieved by raising the temperature to 550°C. On further heating, the particles continued to increase in size and eventually were observed to exhibit mobility on the graphite surface (iron at 750°C and molybdenum at 825°C). It is possible that this action was the result of the creation of monolayer channels across the surface, the presence of which might be difficult to detect in the transmission image. This behavior resulted in both a dramatic increase in average particle size resulting from collision and coalescence processes, and an enhancement in the number of such particles accumulating at the potentially active graphite edge and step sites. In both systems onset of catalytic attack was found to occur at 890°C as these particles were seen to create channels across the basal plane. This action remained the exclusive form of attack up to 1000°C, there being no evidence in these experiments for either pit formation or deposition of extraneous carbonaceous material.

(*c*) *In-Situ Electron Diffraction Analysis*

In a final series of experiments the electron microscope was operated in the *in-situ* diffraction mode and patterns taken of the FeS_2/graphite specimens at various stages of the reaction during heating from room temperature up to 850°C in 0.2 Torr hydrogen. The advantages of using graphite as an internal standard for this type of examination was stressed in a previous study from this laboratory (*14*). Table 1 shows the distribution of possible chemical species which are present during reduction of iron disulfide over the temperature range 240 to 850°C and Figs. 7A–7C show a selection of patterns taken at various stages of the reaction. Examination of the data shows that reduction of FeS_2 to FeS and Fe_7S_8 (Pyrrhotite) starts to occur at 240°C and at 500°C these latter sulfides become the stable phases. On increasing the temperature to 750°C metallic iron (both α and γ phases) begin to appear along with Fe_3C. Dissolved carbon in the respective metallic phases probably has a significant effect on the measured *d*-spacings of the species and may account for the deviations observed from the theoretical values. The sequence of events found with the iron sulfides is similar to that observed in a previous study where this approach was used to follow the progressive reduction of MoS_2 (*10*).

DISCUSSION

In the present investigation dealing with the mechanistic features of the interaction of hydrogen with metal sulfides we have selected single crystal graphite as the medium on which probe reactions are to be conducted. This well characterized material is an ideal candidate for this type of study:

(i) In the absence of a catalyst, the graphite–hydrogen reaction does not proceed at temperatures below 1000°C (*15*).

(ii) Most metals are known to catalyze the reaction at temperatures in excess of 600°C by a channeling mode (*11*).

(iii) The channels are created when the metal particles encounter edges and steps, and generally follow definite crystallographic directions across the graphite basal plane. The channels are predominantly straight and occasionally change directions by 60° and 120°, but always tend to maintain their orientation parallel to the $\{10\bar{1}l\}$ zig-zag faces.

(iv) In contrast to catalytic oxidation reactions of graphite, attack perpendicular to basal plane regions to form pits is an event which is rarely observed in the presence of hydrogen, and,

(v) graphite is a conductor which is not subject to "charging effects" during interaction with the electron beam.

The major feature which emerges from this study is that the interaction of hydrogen with certain metal sulfides produces a species, which even at room temperature is highly reactive towards the π-electrons present on the graphite basal plane and this action leads to the creation of pits. The observation that the carbonaceous solid does not necessarily have to be in direct contact with the metal sulfide particles in order for hydro-gasification to occur, indicates that at the gas pressure used in these experiments, it is possible for the active species to be transported through the gas phase in addition to the surface migration route. The intensity of this action appears to increase with temperature up to a certain point and then come to a complete halt. Catalytic activity could, however, be regenerated by lowering of the temperature to a previously active regime.

This intriguing pattern of behavior can be rationalized according to the following arguments. At low temperature graphite can only undergo attack due to interaction with atomic species, generated from the dissociation of molecular hydrogen with metal sulfides via a reversible chemisorption process. This reaction will continue until conditions are reached which favor weakening of sulfur–metal bonds and the concomitant release of hydrogen sulfide. At higher temper-

TABLE 1

Electron Diffraction Pattern Analysis of FeS_2/Graphite as a Function of Temperature in 0.2 Torr H_2

Temperature (°C)	Calculated d-spacings (nm)	d-spacings					
		FeS_2	FeS	Fe_7S_8	Fe_3C	α-Fe	γ-Fe
240	0.2861	0.2873(011)		0.2873($\underline{2}$22)			
	0.2651		0.2661(112)	0.2639($\bar{2}$24)			
	0.1902	0.1911(121)					
300	0.3939		0.3882(102)				
	0.2908		0.2892(111)				
	0.2680	0.2693(101)	0.2661(112)				
	0.1953	0.1960(006)	0.1953(120)	0.1952(602)			
400	0.3945		0.3882(120)				
	0.2867	0.2873(011)	0.2892(111)	0.2873(222)			
	0.2715	0.2712(020)		0.2734(315)			
	0.1949	0.1941(204)	0.1953(120)	0.1952(602)			
500	0.2944		0.2940(004)				
	0.2727	0.2712(020)		0.2734(315)			
	0.2543		0.2556(104)	0.2545(026)			
	0.2127	0.2117(021)	0.2141(105)				
	0.1974		0.1960(006)	0.1974($\bar{3}$31)			
	0.1698	0.1693(002)	0.1705(031)	0.1695($\bar{3}$37)			
	0.1655		0.1653(032)				
	0.1491		0.1492(220)	0.1486(440)			
600	0.3005		0.2984(110)				
	0.2590		0.2584(200)				
	0.2125		0.2141(015)				
	0.1754		0.1748(123)				
	0.1636		0.1638(116)				
	0.1500		0.1503(125)				
700	0.5099		0.5168(100)				
	0.3077		0.3123(103)				
	0.2623		0.2661(112)				
	0.2126		0.2141(105)				
	0.1765		0.1748(123)				
	0.1653		0.1653(302)				
	0.1513		0.1503(125)				
	0.1304		0.1294(306)				
	0.1060		0.1059(325)				
750	0.3044				0.3044(111)		
	0.2589		0.2584(200)				0.2579(110)
	0.2121						0.2105(111)
	0.2055				0.2056(130)	0.2041(110)	
	0.1743		0.1739(205)				
	0.1644		0.1638(116)		0.1646(310)		0.1631(210)
	0.1506		0.1503(125)		0.1509(003)		
	0.1331		0.1330(224)		0.1331(312)		
	0.1296		0.1294(036)		0.1298(203)		0.1289(220)
	0.1236		0.1227(403)				
800	0.3034				0.3023(111)		
	0.2584		0.2584(020)				0.2579(110)
	0.2151		0.2158(023)				
	0.1864		0.1854(212)				
	0.1701		0.1705(301)				
	0.1541				0.1547(311)		
	0.1319		0.1330(224)		0.1329(123)		
	0.1119		0.1123(141)		0.1116(014)		
850	0.3059				0.3023(111)		
	0.2636		0.2661(112)				
	0.2157		0.2158(023)				
	0.1849		0.1847(115)				
	0.1831		0.1833(016)				
							0.1823(200)

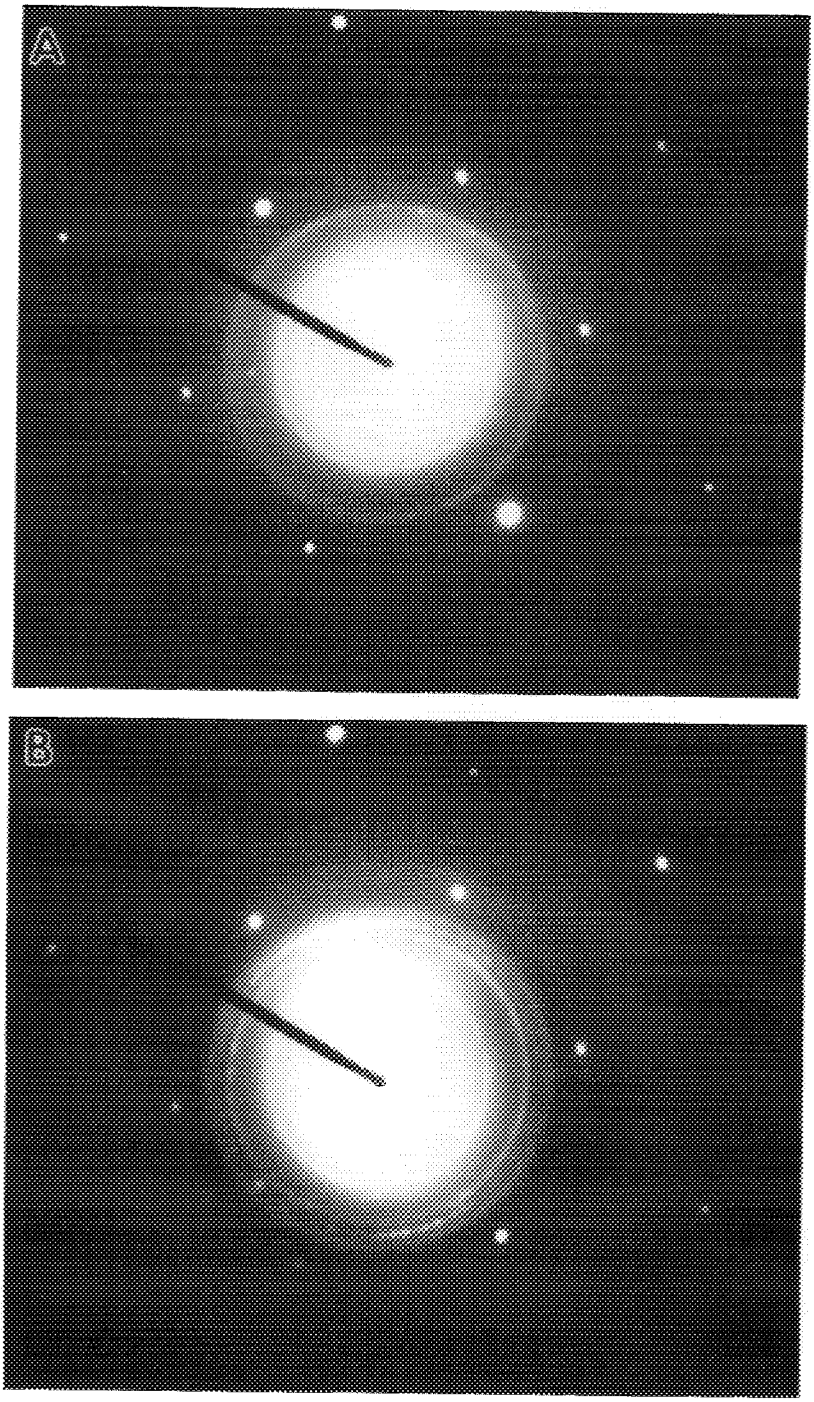

FIG. 7. Electron diffraction patterns of an FeS_2/graphite specimen taken at various temperatures during the interaction with 0.2 Torr hydrogen: (A) 300°C, (B) 500°C, and (C) 750°C.

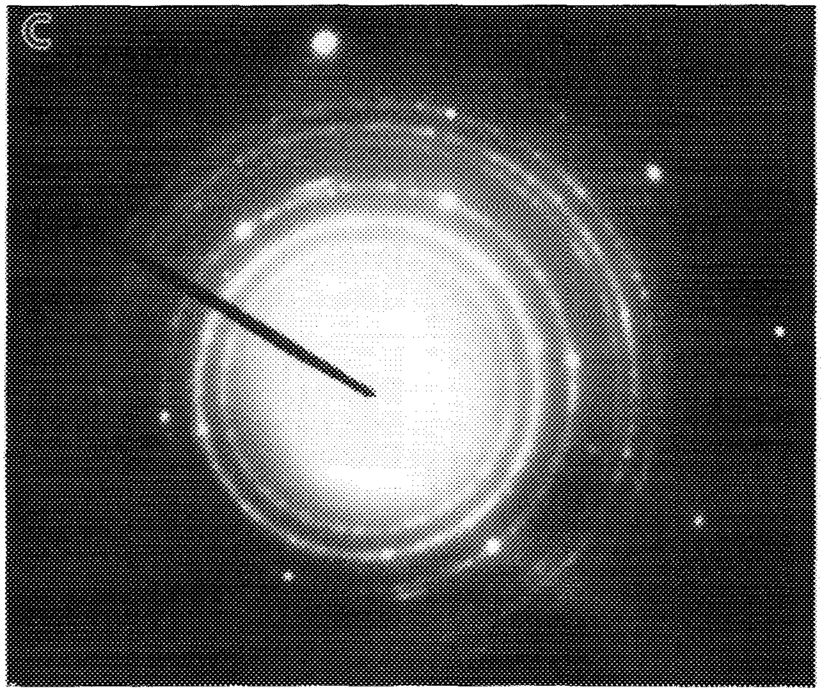

FIG. 7—*Continued*

atures, the sulfides are converted to the metallic state and the mode of gasification of graphite will revert to that normally associated with the metal, i.e., channeling. In this regard, the data obtained from the *in-situ* electron diffraction analysis is extremely relevant in establishing the limitations of the sulfides examined in the present study with respect to their chemical stability at a given temperature. In the case of FeS_2, decomposition into pyrrhotite and/or FeS appears to take place at around 300°C and as a consequence this reaction would interfere with the dissociative hydrogen chemisorption step. A somewhat more extended reactivity range was found with MoS_2, where decomposition into Mo_2S_3 starts at $\sim$450°C (10). On the other hand, decomposition of FeS does not occur until temperatures in excess of 750°C and as a result it is probable that this sulfide will exhibit the widest temperature range for the generation of atomic hydrogen species.

Hydrogen is known to undergo reversible dissociative adsorption on molybdenum disulfide (6–9), and it might be expected that other metal sulfides, including iron sulfide, would exhibit similar chemisorption characteristics. As a consequence, provided that the rate of the recombination step can be minimized such systems may be regarded as atomic hydrogen generators. In order to maximize the utilization of such atomic species in a chemical reaction transportation processes become a major concern. In this regard, it is important to consider the phenomenon of migration or "spillover" of adsorbed species which is known to occur in a number of supported metal catalyst systems.

Pioneering studies by Boudart *et al.* (*16*) demonstrated that hydrogen spillover from hydrogen crystallites to an alumina support took place by migration of atomic species across carbon bridges between the metal and the oxide. In subsequent studies other workers (*17–19*) invoked the phenomenon of hydrogen spillover to account for the finding that platinum could facilitate the hydro-gasification of graphite at temperatures as low as 400°C. There is now abundant evidence in the literature that migration of atomic hydrogen can occur over a variety of surfaces (*20*). Although diffusion of atomic hydrogen through the gas phase has been proposed (*21*), we believe that the dynamic observations reported from the current studies are the first definitive evidence that such process can occur.

The reaction of atomic hydrogen with carbon has been the subject of numerous papers, one of the earliest dating back to 1946 (*22*). In these studies the atomic species were generated either in low pressure microwave discharge units or by dissociation of molecular hydrogen over a heated tungsten filament. There is a general consensus that the reaction between graphite and atomic hydrogen can take place at a relatively rapid rate at room temperature and pressures of up to 2.8 Torr (*23–28*). Wood and Wise (*26*) studied the effect of temperature on the reaction and claimed that the system exhibited an activation energy of 5.5 kcal/mole and went through a maximum at about 525°C.

The changes in appearance of a graphite surface following exposure to atomic hydrogen at 700 to 800°C were examined using optical and scanning electron microscopy techniques by McCarroll and McKee (*27*). They found that hexagonal-shaped pits were produced in the basal plane, the sides of which were oriented parallel to the $\{10\bar{1}l\}$ crystal faces. In more recent studies Yang and co-workers (*29, 30*) used extended Hückel molecular orbital (EHMO) calculations to explain the reactivity of atomic hydrogen formed from thermal dissociation of molecular hydrogen with graphite. From these model studies they showed that the $\{10\bar{1}l\}$ zig-zag faces were more reactive than the $\{11\bar{2}l\}$ armchair faces. This theoretical treatment was complemented with experiments which involved transmission electron microscopy observations of gold decorated graphite specimens which had been reacted in molecular hydrogen for 2 hr at 1435°C. They demonstrated that atomic species produced under these conditions attacked the basal plane regions to create monolayer pits.

The major dilemma encountered in the present work was the progressive build up of carbonaceous deposits on the graphite surface, a feature which became most pronounced at 300°C and could be removed by raising the temperature to 500°C. This finding suggests that during the interaction of atomic species with graphite, the decomposition products contained a selection of high molecular weight hydrocarbons which have a tendency to condense on the specimen surface. In contrast, when metal/graphite systems are heated in hydrogen methane is the sole product and the specimens remain relatively clean throughout the reaction.

It is clear that this approach holds a great deal of potential for the conversion of carbonaceous solids into a variety of extremely useful precursor hydrocarbon molecules. The notion of producing atomic hydrogen via various discharge techniques is extremely interesting and offers the opportunity of controlling the energy of the atomic species, however, this experimental approach is fraught with technical difficulties when one attempts to scale up such a reactor system. The question which arises is can one perform such reactions by generating atomic hydrogen species from a somewhat simpler route, i.e., by catalytic dissociation of molecular hydrogen. The model studies carried out in the present investigation indicate that this is a viable proposition at the low pressures used in the *in-situ* electron microscopy experiments. The verification that similar conversions can be achieved on a larger scale must await the results of further studies.

ACKNOWLEDGMENTS

Financial work for this research was provided by the United States Department of Energy, Basic Energy

Sciences, Grant DE-FG05-89ER14076 and CFFLS program Contract DE-FC22-90-PC90029.

REFERENCES

1. Massoth, F. E., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 27, p. 265. Academic Press, New York, 1978.
2. Delmon, B., *in* "Proc. Climax Third Intern. Conf. on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 73, Climax Molybdenum Co., Ann Arbor, MI, 1980.
3. Grange, P., *Catal. Rev. Sci. Eng.* **21,** 135 (1980).
4. Topsoe, H., and Clausen, B. S., *Catal. Rev. Sci. Eng.* **26,** 395 (1984).
5. Tanaka, K., and Okuhara, T., *in* "Proc. Climax Third Intern. Conf. on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 170, Climax Molybdenum Co., Ann Arbor, MI, 1980.
6. Stevens, G. C., and Edmonds, T., *J. Less-Common Met.* **54,** 321 (1977).
7. Wright, C. J., Sampson, C., Fraser, D., Moyes, R. B., Wells, P. B., and Riekel, C., *J. Chem. Soc. Faraday Trans. I* **76,** 1585 (1980).
8. Polz, J., Zeilinger, H., Müller, B., and Knözinger, H., *J. Catal.* **120,** 22 (1989).
9. Anderson, A., Al-Saigh, Z. Y., and Hall, W. K., *J. Phys. Chem.* **92,** 803 (1988).
10. Baker, R. T. K., Chludzinski, J. J., and Sherwood, R. D., *J. Mater. Sci.* **22,** 3831 (1987).
11. Baker, R. T. K., *in* "Carbon and Coal Gasification" (J. L. Figueiredo and J. A. Moulijn, Eds.), p. 231 NATO ASI Series, No. 105, Martinus Nijhoff, Dordrecht, 1986.
12. Rodriguez, N. M., Oh, S. G., Downs, W. B., Pattabiraman, P., and Baker, R. T. K. *Rev. Sci. Instrum.* **61,** 1863 (1990).
13. Hennig, G., *in* "Chemistry and Physics of Carbon" (P. L. Walker, Jr., Ed.), Vol. 2, p. 1 Dekker, New York, 1966.
14. Oh, S. G., and Baker, R. T. K., *J. Catal.* **128,** 137 (1991).
15. Walker, P. L. Rusinko, F., and Austin, L. G., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.) Vol XI, p. 133, Academic Press, New York, 1959.
16. Boudart, M., Aldag, A. W., and Vannice, M. A., *J. Catal.* **18,** 46 (1970).
17. Tomita, A., and Tamai, Y., *J. Catal.* **27,** 293 (1972).
18. Olander, D. R., and Balooch, M., *J. Catal.* **60,** 41 (1979).
19. Chang, T. S., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **123,** 486 (1990).
20. Pajonk, G. M., Teichner, S. J., and Germain, J. E., (Eds.), "Spillover of Adsorbed Species," Studies in Surface Science and Catalysis No. 17, Elsevier, Amsterdam, 1983.
21. Baumgarten, E., Lentes-Wagner, C. and Wagner, R., *J. Catal.* **117,** 533 (1989).
22. Avramenko, L. E., *Zh. Fiz. Khim.* **20,** 12999 (1946).
23. Blackwood, J. D., and McTaggart, F. K., *Aust. J. Chem.* **12,** 533 (1959).
24. Gill, P. S., Toomey, R. E., and Moser, H. C., *Carbon* **5,** 43 (1967).
25. Vastola, F. J., Walker, P. L., Jr., and Wightman, J. P., *Carbon* **1,** 11 (1963).
26. Wood, B. J., and Wise, H., *J. Phys. Chem.* **73,** 1348 (1969).
27. McCarroll, B., and McKee, D. W., *Carbon* **9,** 301 (1971).
28. Gesser, H. D., and Czubryt, J. J., *Fuel* **67,** 375 (1988).
29. Chen, J. P., and Yang, R. T., *Surf. Sci.* **216,** 481 (1989).
30. Pan, Z. J., and Yang, R. T., *J. Catal.* **123,** 206 (1990).