JOURNAL OF CATALYSIS **110**, 74–81 (1988)

Controlled Atmosphere Electron Microscopy Study of the Gasification of Graphite by Water, Hydrogen, and Oxygen Catalyzed by a Nickel/Potassium Mixture

J. CARRAZZA,*,† J. J. CHLUDZINSKI, JR.,‡ H. HEINEMANN,*,§ G. A. SOMORJAI,*,† AND T. K. BAKER‡,[1]

Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, and Departments of †Chemistry and §Chemical Engineering, University of California, Berkeley, California 94720; and ‡Corporate Research Science Laboratories, Exxon Research and Engineering Company, Clinton Township, Route 22 East, Annandale, New Jersey 08801

Received April 7, 1987; revised September 30, 1987

The gasification of graphite by H_2O vapor, wet H_2, and wet O_2, catalyzed by a Ni/K mixture is studied using controlled atmosphere electron microscopy (CAEM). In H_2O vapor the carbon consumption, between 550 and 1100°C, is catalyzed by an edge recession mode of attack in the $[11\bar{2}0]$ direction, with no sign of deactivation. An activation energy of 30.8 ± 0.9 kcal/mol is obtained in this case. This value is similar to those obtained in kinetic studies of the steam gasification of both graphite and char, using this catalyst. In wet H_2 both channeling and edge recession occur simultaneously. The activation energy obtained is equal to 30 ± 2 kcal/mol. The catalyst deactivates above 1000°C, but can be regenerated by treating the sample in H_2O vapor at 600°C. In wet O_2, graphite is also gasified by edge recession, but no preferred direction is observed. The catalyst maintains its activity up to 1000°C, and an activation energy of 25 ± 2 kcal/mol is obtained. These results show that the catalytic properties of the Ni/K mixture are superior to those of Ni and K alone due to a cooperative effect between the components.

INTRODUCTION

Recently (*1, 2*), we reported that mixtures of KOH and various transition metal salts were good catalysts for the steam gasification of graphite and char. These catalysts promote the formation of H_2 and CO_2 above 550°C, and have a high resistance to deactivation. Out of all the catalysts studied, the one derived from a mixture of KOH and $Ni(NO_3)_2$ has the best kinetic properties for this reaction. This catalyst, denominated from now on as Ni/K catalyst, shows the highest activity for H_2 production at 580°C (1.2 ml H_2/min) and a relative low activation energy (~30 kcal/mol).

In this work we used controlled atmosphere electron microscopy (CAEM) to characterize this catalyst in further detail. We studied the interaction between the Ni/K catalyst and graphite surfaces in three gas environments; H_2O vapor, H_2/H_2O, and O_2/H_2O. This technique is an excellent tool to study the surface mobility and wetting properties of the catalyst. It also allows the determination of the mode of attack of the gaseous reactants to the graphite lattice, promoted by the catalyst, and the intrinsic rates of carbon consumption. This characteristic is very important because comparisons of the activities of various catalysts can be made, without the interference of geometric effects, such as surface area or number of active sites.

In this article, our goal is to show that the Ni/K catalyst has distinctive morphological and kinetic properties for carbon gasification. We will describe and discuss these properties in the three gas environments studied, and then compare them to those reported earlier for KOH or Ni metal (*3–6*),

---

[1] Permanent address: Department of Chemical Engineering, Auburn University, AL 36849.

0021-9517/88 $3.00

placing emphasis on the advantage of the mixture over the components used alone. We conclude that these advantages are due to a cooperative effect between Ni and K.

EXPERIMENTAL

A detailed description of the CAEM technique can be found elsewhere (*7*). Ni and K are introduced onto transmission specimens of natural single crystal graphite (Ticonderoga, NY) as an atomized spray, using 0.1% solutions of $Ni(NO_3)_2$ and KOH. Samples were then dried in air and introduced into the environmental cell.

Before the sample was exposed to the reactant gases, it was heated in Ar at 450°C for 30 min to decompose the $Ni(NO_3)_2$ and achieve a good metal particle nucleation. Particles grew to an average size of 15 nm in diameter.

The gases used, Ar, H_2, and O_2, were obtained from Scientific Gas Products, Inc., with stated purities of 99.999%, and were used without further purification. H_2O vapor was introduced into the system by allowing a carrier gas to flow through a bubbler containing deionized H_2O at 20°C. This procedure produces a gas/H_2O ratio of ~40/1 in the gas reaction cell.

RESULTS

The Nickel–Potassium/Graphite–Water Vapor System

After graphite samples loaded with KOH and $Ni(NO_3)_2$ were treated at 450°C in Ar, particle nucleation was observed on both the basal and the edge planes. When the sample was treated in a water vapor environment (2 Torr Ar : H_2O 40 : 1), the particles located on the graphite edge region underwent a transformation from nonwetting condition to wetting condition between 475 and 525°C. They spread over the whole edge area and formed a very thin film that became very difficult to observe. This suggests that the film width is of the order of the apparatus resolution (2.5 nm).

On continued heating to 555°C these re-

FIG. 1. Sequence of photographs taken from the CAEM video display, showing the edge recession attack of carbon in H_2O vapor at 900°C. The time between (A) and (B) is 3 sec.

gions started to erode, giving a ragged appearance to the initially uniform edges. The carbon erosion developed into a more ordered edge recession as the temperature approached 675°C. Figures 1A and 1B show a two-picture sequence illustrating this mode of attack.

The edge recession involved the whole area and the various fronts of attack where separated by 60° angles, in the direction parallel to the $[11\bar{2}0]$ crystallographic orientation of the graphite structure. The orientation was determined by referring the position of the fronts of attack to that of twin bands, which are always present in the graphite in the $[10\bar{1}0]$ direction.

The rate of edge recession increased continuously when the temperature was raised from 675 to 1100°C, and no evidence of deactivation was observed. A quantitative analysis of the rates of edge recession as a function of temperature is shown in Fig. 2 in the form of an Arrhenius plot. An activation energy of 30.8 ± 0.9 kcal/mol was obtained. This value is consistent with the one obtained from kinetic studies using a flow reactor system (*1*).

At temperatures above 955°C, occasionally, a change in the mode of attack was observed. The film responsible for the edge recession sintered into small particles that promoted the formation of channels. This phenomenon may be caused by a change in the characteristics of the catalyst brought about by a buildup of H_2 product in the gas environment. This is in agreement with the results described in the following section.

The Nickel–Potassium/Graphite–Wet Hydrogen System

The catalytic effect of Ni/K mixtures on the gasification of graphite on a $H_2:H_2O$ 40:1 atmosphere was studied on samples that had been either gasified in steam at 1000°C or heat treated in Ar at 450°C. The results in both cases were identical, and they will be described without making reference to the sample pretreatment.

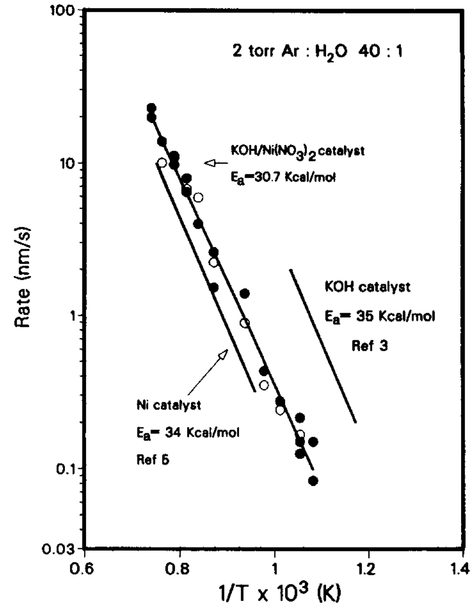

FIG. 2. Arrhenius plot of Ni/K catalyzed edge recession rates of graphite in 2 Torr of wet Ar. The filled circles represent the results obtained after heat treating the sample in Ar for 30 min at 450°C. The open circles represent the results obtained after treating the sample in 2 Torr of wet H_2 at 1100°C. Results previously reported for KOH and Ni metal are included for comparison purposes. The length of the curves indicates the temperature range studied.

The first signs of catalytic attack when the specimens were heated in 2.0 Torr of wet H_2 were observed at 545°C. It took the form of relatively straight channels which were created by catalyst particles that had nucleated along the edges of graphite.

When first formed the channels remained parallel-sided, and as the temperature was raised to 565°C, they started to acquire a fluted appearance. This is the result of active catalyst particles spreading along the channel walls, which then proceeded to catalyze the reaction by an edge recession mode. (See region indicated by arrows in Figs. 3A and 3B.)

On raising the temperature to 675°C many of the previously inactive particles located on the graphite basal plane started to exhibit mobility. When these particles encountered an edge they underwent a rapid spreading action and this resulted in a sub-

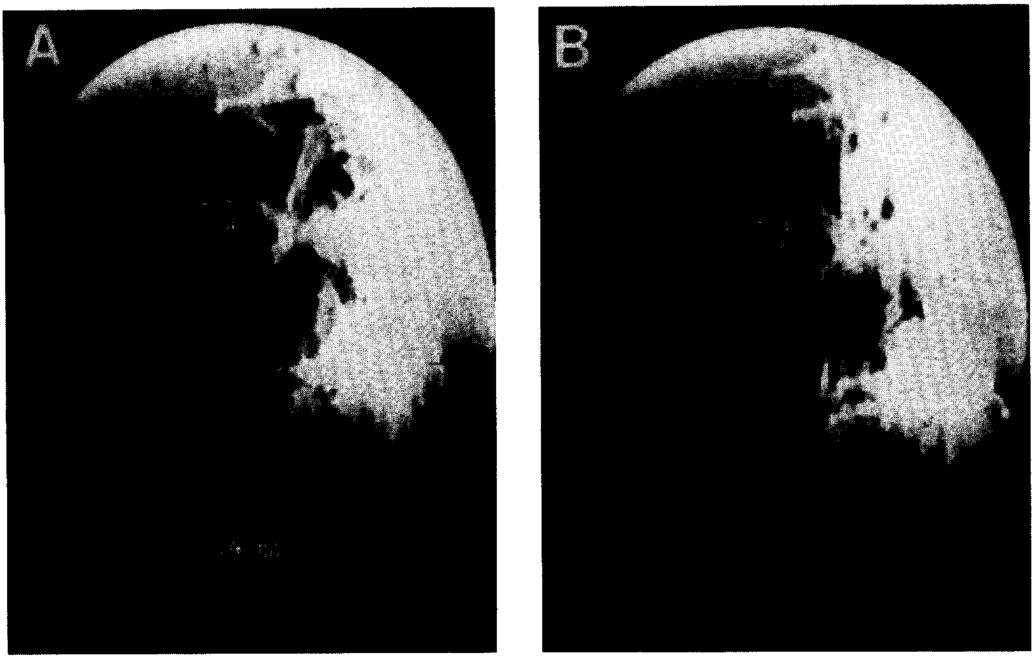

FIG. 3. Sequence of photographs, showing the modes of attack in 2 Torr of wet H_2. The region indicated by the arrows shows the recession of the channel walls, as described in the text (see results). Also note the simultaneous carbon attack by edge recession and channeling in the lower part of the photographs. The time between (A) and (B) is 1 sec.

sequent removal of carbon by edge recession in directions parallel to the $[11\bar{2}0]$ crystallographic orientation. The variation in edge recession rate with temperature was determined and the data are presented in Fig. 4 in the form of an Arrhenius plot. An activation energy of 30 ± 2 kcal/mol was obtained from the slope of this line.

Both modes of attack, edge recession and channeling, were occurring simultaneously during the whole temperature range studied (600–1100°C). Below 900°C the channels were very short and were usually taken over by the progress of the recession of neighbor edges. As the temperature was raised to 1100°C the edge recession tended to slow down and in some regions it stopped completely, leaving channeling as the only mode of attack.

The edge recession activity could be regenerated by treating the sample in wet Ar at about 600°C. The wet H_2 treatment did not affect the properties of the Ni/K mixture for promotion of the edge recession mode of attack of steam. Figure 2 shows that the rates of edge recession obtained in wet Ar after a H_2/H_2O treatment (open circles), are identical to those obtained after a heat treatment in Ar (filled circles).

The Nickel–Potassium/Graphite–Wet Oxygen System

Treatment of nickel/potassium specimens in 2.0 Torr of wet O_2 ($O_2 : H_2O$ 40 : 1) at 605°C resulted in the formation of shallow channels. During this stage of the reaction, channels followed random pathways and no erosion of the walls was observed.

As the temperature was raised above 665°C, particle mobility increased. Particles that came into contact with edges immediately underwent spreading and the coated edges started to recess. At the same time, catalyst particles at the head of channels previously formed gradually spread along

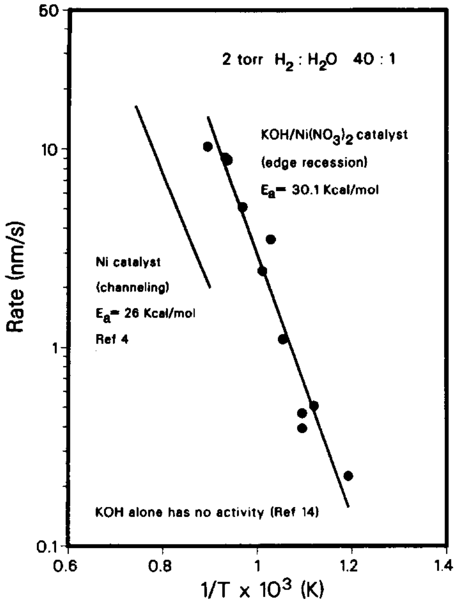

FIG. 4. Arrhenius plot of Ni/K catalyzed edge recession rates of graphite in 2 Torr of wet H_2. The results previously obtained for the channeling mode of attack of Ni metal are included for comparison. The length of the curves indicates the temperature range studied.

the walls, which then proceeded to expand laterally (see Fig. 5).

In contrast with the behavior observed in wet H_2 and wet Ar, the recession in wet O_2 did not appear to follow any preferred direction. Also, in this case the catalyst attack continued up to 1015°C, there being no evidence for deactivation of the gasifying edges. From an Arrhenius plot of the variation of the edge recession with temperature, an activation energy of 25 ± 3 kcal/mol was obtained (see Fig. 6).

DISCUSSION

The Ni/K mixture catalyzes the gasification of graphite in both reducing and oxidizing environments. The carbon consumption in all cases occurs at the catalyst/carbon interface and the gas mode of attack is affected by the morphology of the mixture on the surface. In wet Ar and wet O_2 the catalyst spreads and promotes the carbon attack by an edge recession mode. In wet H_2 the catalyst is present in both a wetting and

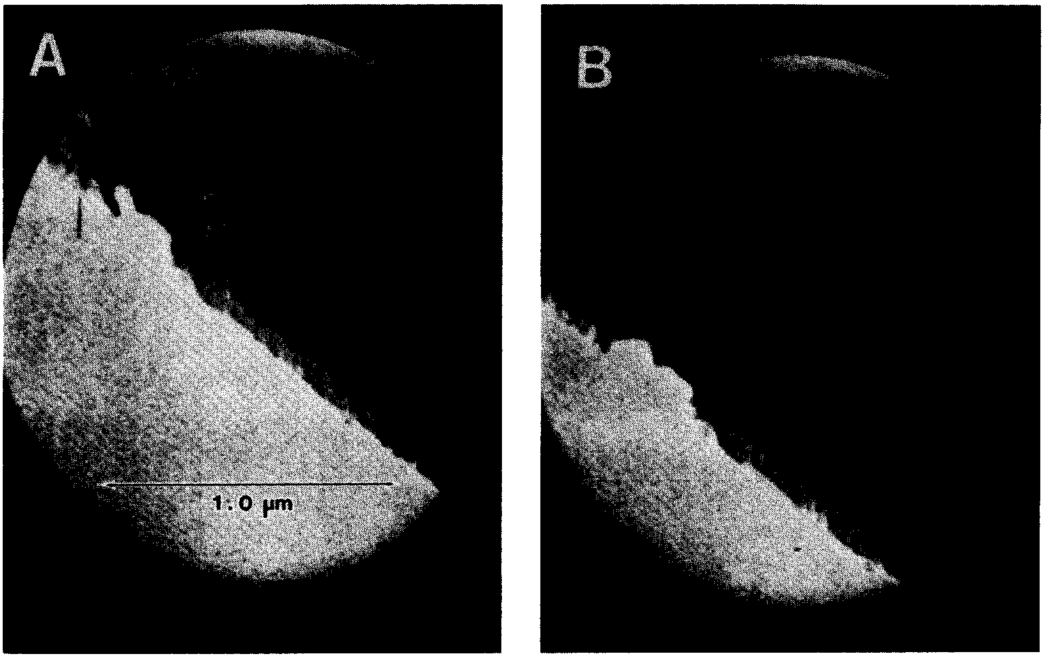

FIG. 5. Sequence of photographs in wet O_2 at 650°C, showing the irregular channels formed before catalyst spreading. Note also the erosion of the edges, which is the first indication of edge recession attack. The time between photographs is 10 sec.

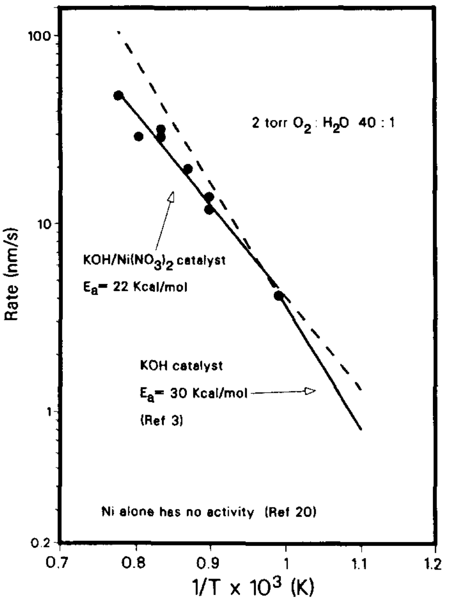

FIG. 6. Arrhenius plot of Ni/K catalyzed edge recession rates of graphite consumption in 2 Torr of wet O_2. The results previously obtained for KOH are included. The length of the curves indicates the temperature range studied. The dotted lines are extensions of the curves, included to facilitate the comparison.

a spreading condition, and the gasification occurs simultaneously by channeling and edge recession.

The surface tension forces among the carbon substrate (solid), the catalyst (liquid), and the gas environment control the wetting properties of the catalyst, and are responsible for the different modes of attack observed. The catalyst spreads over the carbon surface, and favors edge recession, because the sum of the surface tensions at the catalyst–substrate (γ_{sl}) plus catalyst–gas (γ_{lg}) interfaces is lower than the surface tension at the gas–substrate interface (γ_{sg}),

$$\gamma_{sg} > \gamma_{lg} + \gamma_{sl}. \qquad (1)$$

This is the case in H_2O vapor and O_2/H_2O environments, but there are differences in catalyst behavior between these two cases. In wet O_2, at 500°C, the catalyst forms particles that only wet the carbon surface, and as the temperature rises above 650°C these particles spread over the edge planes. In wet Ar the opposite behavior is observed. The catalyst spreads at temperatures as low as 500°C, and as the temperature approaches 1000°C, particle nucleation takes place.

Changes in the interface interactions due to chemisorbed species on the carbon surface and/or oxidation state of the catalyst can be responsible for this difference. In wet O_2, the edge surfaces of graphite are covered with oxygen-containing species (*8*, *9*). This lowers the gas–solid surface tension (γ_{sg}) to such a level that Eq. (1) is no longer satisfied, and particle nucleation is favored. These species desorb from the surface between 600 and 700°C (*8*, *9*), and since the surface free energy of clean edge planes of graphite is much higher than that of the catalyst (*10*, *11*), spreading now becomes favored. In H_2O vapor, below 650°C the catalyst interacts with a larger fraction of clean edges than that in the O_2 case because the sticking coefficient of water on graphite is much smaller than that of O_2 (*8*). For this reason, in the wet Ar case the catalyst spreading over the edge surfaces is observed as soon as the Ni/K mixture becomes mobile. As the temperature approaches 1000°C, H_2 formed in the carbon–water reaction builds up in the cell. This changes the wetting properties of the catalyst, and favors particle nucleation.

A second difference between these two cases is the direction of the edge recession attack. In wet O_2 the edge recession does not follow a particular orientation, while in wet Ar this mode of attack occurs only parallel to the $[11\bar{2}0]$ crystallographic direction. A preferred orientation for the gasification of graphite in various gas environments has been reported for many catalysts (*11*). At this point the reasons for this preferential direction are not well understood. Several suggestions have been made in the literature, but they do not explain all the cases studied. It has been suggested (*12*) that because steam adsorbs preferentially at "arm chair" sites (*13*), the carbon gasification is favored in a $[11\bar{2}0]$ direction, but this is not always the case, since there are several cases in which transition metals catalyze the water attack of carbon in the $[10\bar{1}0]$ direction. It has also been suggested (*11*) that the affinity of the catalyst to a particular edge face is the driving force for the gasification in that direction, but our observations indicate that the catalyst is spread over the whole edge area and carbon attack is only promoted in a particular direction.

In wet H_2, between 600 and 1000°C, both edge recession and channeling modes of attack are observed simultaneously, because a fraction of the catalyst spreads upon the edges, while the rest only wets them. The channeling attack is probably due to Ni metal, since the characteristics observed in our study are very similar to those reported previously when Ni was deposited alone on graphite (*4*). The edge recession, on the other hand, can only be explained as the result of the interaction between Ni and K, because Ni deposited alone does not show any evidence for this mode of attack in wet H_2 (*4*) and K salts are not active for carbon gasification in reducing environments (*14*). Furthermore, this mode of attack has not been previously reported in reducing environments. This interaction is suppressed above 1000°C in H_2, and can be regenerated by treating the sample in H_2O vapor at 600°C, as shown in Fig. 2.

The catalytic properties of the Ni/K mixture for carbon gasification are superior to those of Ni or K alone. In the H_2O vapor–graphite reaction the clearest advantage of the Ni/K mixture is its resistance to poisoning. CAEM (*3,5*) and flow reactor (*15, 16*) studies show that both K and Ni deactivate when used as catalysts for steam gasification of graphite below 725°C. On the contrary, this study shows that the Ni/K mixture does not show any sign of deactivation in wet Ar up to 1100°C. This result is in agreement with flow reactor studies reported elsewhere (*1*). In wet H_2 the intrinsic activity of the Ni/K mixture is two times higher than that reported for Ni alone, while K salts are inactive. Furthermore, the Ni/K mixture favors an edge recession mode of attack and Ni alone promotes channeling; therefore the difference in total rate of carbon consumption should be even higher. In wet O_2 the rates of edge recession for K alone and Ni/K are similar and neither of them deactivate. There are differences, however, between these two systems. The activation energy in the Ni/K case (22 kcal/mol) is lower than that reported for K alone (30 kcal/mol), and even though both promote an edge recession mode of attack for the O_2–graphite reaction, in the Ni/K case there is no preferential direction of attack, while in the case of K alone the carbon consumption occurs parallel to the $[10\bar{1}0]$ direction.

The distinct catalytic properties of the Ni/K mixture are due to a cooperative effect between the components. In the case of steam gasification this conclusion is also supported by flow reactor studies in both graphite and char (*1, 2*). This cooperative effect has also been observed in other systems. In steam only, CAEM studies of Pt/Ba (*17*) indicate that this mixture is more resistant to poisoning than the components used independently, and flow reactor studies of $Fe(NO_3)_3/Na_2(CO_3)$ mixtures (*18*) show that this catalyst is more active than either $Fe(NO_3)_3$ or $Na_2(CO_3)$ alone. In wet H_2, mixtures of K_2SO_4 and $FeSO_4$ form a molten phase at 650°C and this phase has a higher steady-state activity and a more improved CH_4 selectivity than those of the components used alone (*19*).

A CAEM study of the catalytic activity of Ni/Ca mixtures for carbon gasification in wet Ar was reported previously (*5*). This catalyst shows several similarities with the Ni/K catalyst for the H_2O vapor–graphite reaction. The catalytic properties of the Ni/Ca mixture, as in the case of Ni/K, can only be explained by the interaction between the components. Both systems spread over the edge surfaces of carbon between 500 and 600°C, and they both promote an edge recession mode of attack in the $[11\bar{2}0]$ orientation. Also, both systems maintain their activity at high temperatures and no sign of deactivation was observed. Ni/K, however, is more active than Ni/Ca and it has a much lower activation energy.

SUMMARY

We studied the catalytic properties of Ni/K mixtures in H_2O, H_2/H_2O, and O_2/H_2O atmospheres by CAEM. In H_2O and O_2/H_2O environments an edge recession mode of attack is favored, and no sign of deactivation is observed. In H_2/H_2O both edge recession and channeling occur simultaneously and the catalyst deactivates above 1000°C. This mixture shows catalytic properties superior to those of either Ni or K used independently, due to a cooperative effect between the components.

ACKNOWLEDGMENTS

This work was supported by the Assistant Secretary for Fossil Energy, Office of Management Planning and Technical Coordination, Technical Coordination Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098, through the Morgantown Energy Technology Center, Morgantown, WV 26505. The authors gratefully acknowledge the Exxon Research and Engineering contribution, for the use of their facilities and personnel. J. Carrazza acknowledges CEPET of Venezuela for a research fellowship.

REFERENCES

1. Carrazza, J., Tysoe, W. T., Heinemann, H., and Somorjai, G. A., *J. Catal.* **96,** 234 (1985).
2. Carrazza, J., Pandé, R., Sullivan, D. J., Heinemann, H., and Somorjai, G. A., submitted for publication.
3. Mims, C. A., Chludzinski, J. J., Jr., Pabst, J. K., and Baker, T. R. K., *J. Catal.* **88,** 97 (1984).
4. Baker, R. T. K., and Sherwood, R. D., *J. Catal.* **70,** 198 (1981).
5. Baker, R. T. K., and Chludzinski, J. J., Jr., *Carbon* **23,** 635 (1985).
6. Coates, D. J., Evans, J. W., Cabrera, A. L., Somorjai, G. A., and Heinemann, H., *J. Catal.* **80,** 215 (1983).
7. Baker, R. T. K., and Harris, P. S., *J. Sci. Instrum.* **5,** 793 (1972).
8. Kelemen, S. R., and Freund, H., *Carbon* **23,** 619 (1985).
9. Kelemen, S. R., and Freund, H., *Carbon* **23,** 723 (1985).
10. Abrahamson, J., *Carbon* **11,** 337 (1973).
11. Baker, R. T. K., Dumesic, J. A., and Chludzinski, J. J., Jr., *J. Catal.* **101,** 169 (1986).
12. Baker, R. T. K., Lund, C. R. F., and Chludzinski, J. J. Jr., *J. Catal.* **87,** 255 (1984).
13. Magne, P., and Duval, X., *Carbon* **11,** 475 (1973).
14. Long, F. J., and Sykes, K. W., *J. Chem. Phys.* **47,** 361 (1950).
15. Dellanay, F., Tysoe, W. T., Heinemann, H., and Somorjai, G. A., *Carbon* **22,** 401 (1984).
16. Lund, C. R. F., *J. Catal.* **95,** 71 (1985).
17. Lund, C. R. F., Chludzinski, J. J., Jr., and Baker, R. T. K., *Fuel* **64,** 789 (1985).
18. Suzuki, T., Mishima, M., Takahashi, T., and Watanabe, Y., *Fuel* **64,** 661 (1985).
19. Adler, J., Hüttinger, J., and Minges, R., *Fuel* **63,** 1397 (1984).
20. Baker, R. T. K., *Carbon* **24,** 715 (1986).