JOURNAL OF CATALYSIS **81**, 239–246 (1983)

# Promotion of Nickel-Catalyzed Hydrogasification of Carbon by Alkaline Earth Compounds

TETSUYA HAGA[1] AND YOSHIYUKI NISHIYAMA

*Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai 980, Japan*

Received October 5, 1982; revised December 27, 1982

A pitch coke was impregnated with nickel nitrate and some additives and gasified in an atmospheric hydrogen flow, to investigate the possibility of promoting nickel-catalyzed hydrogasification by the addition of foreign components. Alkaline earths and aluminum nitrate, which were not direct catalysts for the hydrogasification of carbon, enhanced methane formation markedly, while nitrates of potassium, chromium, and iron and also potassium carbonate had almost no effect. Additives which are effective are believed to be in the form of an oxide. In the presence of nickel, methane is formed at two separate regions: 400–700°C and above 750°C. All the promoters increased conversion in the lower temperature reaction while only calcium salt enhanced it in the higher temperature reaction. Promoters, especially magnesium, extensively suppressed the sintering of nickel. The enhancement of methane formation at lower temperatures is ascribed to the increased dispersion of nickel. Possible reasons for the promotions are discussed.

## INTRODUCTION

Catalysis in the gasification of carbons and coals is of potential importance for fuel technology (*1*). At the same time, it offers some interesting fundamental problems which need to be clarified. Hydrogasification of carbon impregnated with nickel catalyst is known to yield methane at two stages (*2–6*). These reactions differ from each other in several features; temperature range, durability, pressure dependence, and so forth (*2, 5, 6*). The reaction occurring at 400–700°C ceases with an increase in temperature; the deactivation is tentatively ascribed to the aggregation of nickel particles (*5, 6*), though the mechanism of the reaction has not yet been elucidated.

If the sintering of the catalyst is the main cause of the deactivation, there is a possibility that the prevention of sintering in some manner would enhance the activity of the catalyst. In the case of a metal catalyst supported by oxides such as silica and alumina, the addition of some compounds is reported to have suppressed the sintering (*7–12*). Although the state of a catalyst supported by the carbon which is to be gasified would differ from that of a normally supported catalyst, it would seem worthwhile seeing whether or not the addition of some compound has any influence upon nickel catalyst hydrogasification. This report describes the result of such a study using a model carbon.

## EXPERIMENTAL

*Carbon specimen.* A calcined pitch coke supplied by Nittetsu Chemical Industrial Company was used in the present study as a model carbon, since it had low reactivity toward hydrogasification without a catalyst and had a relatively small ash content, 0.24 wt%, the major constituents of which were silica and alumina. No appreciable amounts of metallic constituents were found by X-ray microanalysis. The pitch coke was crushed to 32–60 mesh, heated gently in air at 400°C, and poured into cold water. This pretreatment is found to be effective in increasing the catalytic activity of nickel for hydrogasification without a significant change in the surface area. Details of the effect of surface state on gasification are

---

[1] To whom all correspondence should be addressed.

0021-9517/83 $3.00

reported elsewhere (*13*), together with some other methods of activation which will be referred to below.

*Catalyst loading.* The carbon specimens were simultaneously impregnated, unless otherwise stated, with nitrates of nickel and another element from an aqueous solution. After drying, a specimen was heated in a flow of hydrogen up to 300°C, to reduce the nickel. The amounts of nickel and the additives are expressed in weight percentage of metallic element to carbon, irrespective of the working state of the catalyst. The amounts of catalysts given in the results are of nominal value; i.e., the amount used at the time of impregnation.

*Hydrogasification.* Hydrogasifications were normally conducted in a temperature-programmed mode, in which 1.5 g of specimen, packed in a quartz tube of 15 mm i.d., was heated at a rate of 5°C/min up to 1000°C in an atmospheric flow of pure hydrogen (100 ml/min). Methane formation was followed by gas chromatograph analysis of the effluent gas every 3 min. The rates of methane formation are expressed on a carbon basis; i.e., weight of carbon in the methane per minute per weight of carbon remaining, assuming that the methane is the sole carbon-containing product.

## RESULTS

### *General Feature of the Promotion*

The methane formation profiles in nickel-catalyzed hydrogasifications are given in Fig. 1. Methane formation without nickel is negligibly small (less than 0.1% in conversion, as compared with 2.0% in the case of 5% Ni without additive), so that the reactions dealt with here are totally catalytic. In the case of nickel catalyst without additive, methane is formed in two separate regions, which are designated lower temperature reaction (LTR) and higher temperature reaction (HTR), as indicated in the figure.

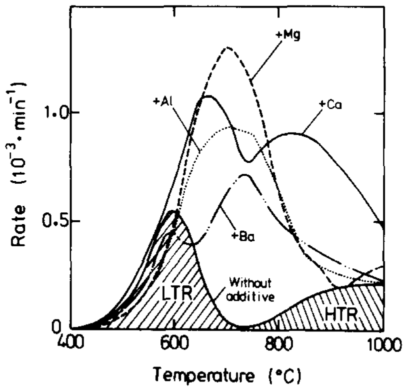

FIG. 1. Methane formation profiles in temperature-programmed hydrogasification. Heating rate: 5°C/min; amount of nickel: 5%; amount of additives: 1% (in the case of Ba, about 0.2% was actually impregnated).

The addition of magnesium, calcium, barium, and aluminum compounds enhanced the methane formation markedly in the manner characteristic to each compound. The large peaks in Ni–Mg, Ni-Ba, and Ni-Al catalysts are the enhanced LTR, while in Ni-Ca catalyst both LTR and HTR are enhanced in the separate regions. The discrimination of LTR and HTR is based on the kinetic feature of the reactions, i.e., whether the reaction is transitory or lasting. Other salts examined but of slight promoting effect are nitrates of iron, chromium, and potassium, and potassium carbonate. Some of those showed a slight suppressing effect against nickel catalysis.

Since it has been ascertained that the additives mentioned above do not in themselves catalyze hydrogasification, they are called "promoters" hereafter. In this report, attention is paid mainly to the action of alkaline earth compounds, especially to those of magnesium and calcium.

### *Effect of the Composition of the Catalyst Systems*

The effect of the amount of promoter was examined with a fixed amount of nickel (5%) and the resultant methane formation profiles are given in Fig. 2 (Ni-Mg) and Fig. 3 (Ni-Ca). The addition of a relatively small amount of magnesium salt increased methane formation quite remarkably, but the effect diminished when the amount of the salt added was increased. In addition, it should

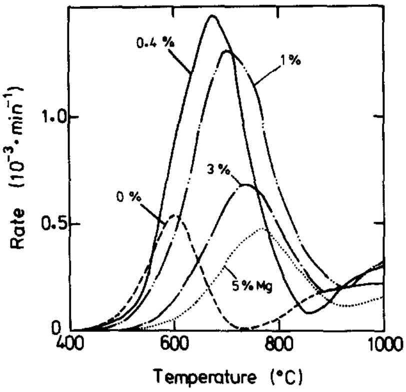

FIG. 2. Methane formation with Ni-Mg catalyst. Amount of nickel: 5%; amount of magnesium: given in the figure.

be noted that methane formation at the lower end of LTR was progressively suppressed by the addition of the magnesium salt, irrespective of the enhancement in total conversion. A similar, but less pronounced, phenomenon was noted in the case of Ni-Ca catalyst. The most remarkable feature in Ni-Ca catalyst is the HTR enhancement by calcium, with the magnitude being almost independent of the amount of the addition. The manner in which LTR was enhanced by Ni-Ca resembled that in which it was enhanced by magnesium.

The effects of the addition of 1% of magnesium and calcium salts to 1% nickel are shown in Fig. 4, which indicates that although enhancement is rather small as compared to cases with 5% nickel, the features are not very different.

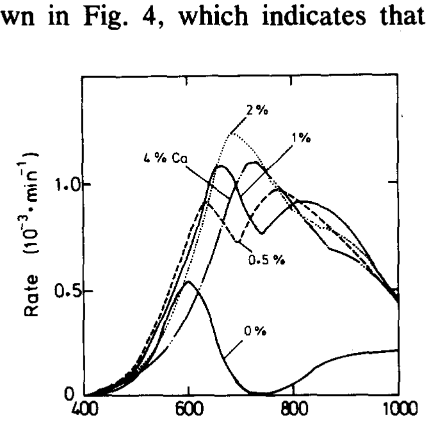

FIG. 3. Methane formation with Ni-Ca catalyst. Amount of nickel: 5%; amount of calcium: given in the figure.

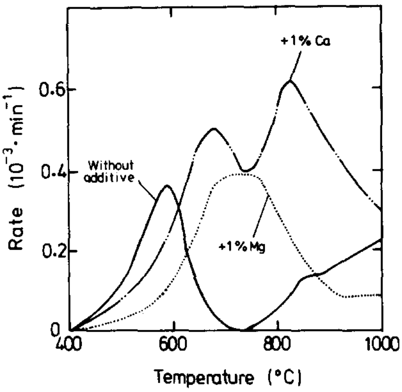

FIG. 4. Methane formation in cases of 1% Ni.

## *Effect of Surface State of Carbon*

The examinations described above were conducted with a surface-modified carbon. By altering the pretreatment conditions, carbons of different surface states and, therefore, of different reactivities, can be prepared. Those which were heated at 400°C in air for various length of time and then poured into cold water were designated WPC. Those heated in hydrogen at 900°C were designated HPC. Using some of these, the effect of the promoters was examined. The conversions in LTR are plotted against the amount of magnesium for five carbons in Fig. 5. The intercepts in the ordinate signify the reactivity of each carbon for catalytic gasification without promoters. The conversion increased with the same slope for each nickel content, and leveled-off at 0.2–0.5% of magnesium. Figure 2, in which the reactivity of B(5) specimen in Fig. 5 is plotted, shows that further addition of magnesium suppressed the reaction. The maximum conversion seems to be higher for carbons of a higher reactivity. The results indicate that the effect of the promoter is not limited to a particular state of carbon, although the manner of promotion varies somewhat with the state of carbon. The effect of calcium on nickel-catalyzed hydrogasification of coal chars and an

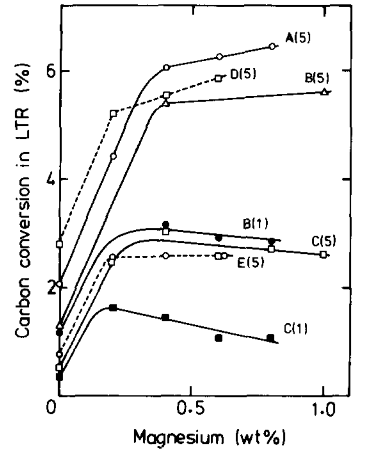

FIG. 5. Effect of magnesium on carbon conversion of different carbons. The numbers in parentheses represent the amount (percentage) of nickel. A, WPC (surface area = 3.0 $m^2/g$); B, WPC (1.0 $m^2/g$); C, WPC (0.5 $m^2/g$); D, HPC (3.0 $m^2/g$); E, HPC (0.5 $m^2/g$).

activated carbon will be reported elsewhere.

*Isothermal Reactions*

To clarify the action of the promoters, the temperature-programmed mode was stopped in the midst of the reaction and the isothermal mode methane formation was analyzed. The results of the Ni-Mg system are given in Fig. 6. The decrease in the methane formation rate became slower as the amount of the addition increased, although the manner of deactivation is still characteristic of LTR. The slower deactivation suggests a slower sintering of nickel, if the sintering is the main reason of the deactivation. In Fig. 7, where a case of 5% Ni + 1% Ca is given, the decrease at 650°C again shows this is a part of LTR, whereas the reaction at 750°C is mostly lasting; i.e., this is in a region of HTR. It can be seen from Fig. 1 that the reaction at 750°C is almost negligible without the promoter.

*Examinations of the State of Catalysts*

The state of the alkaline earth component of the dual catalysts was examined using thermogravimetry. The carbon was impregnated with the promoter without nickel and heated in hydrogen. The weight decrease indicated the following course of decomposition.

$$Mg(NO_3)_2 \xrightarrow{380°C} MgO$$

$$Ca(NO_3)_2 \xrightarrow{500°C} CaCO_3 \xrightarrow{670°C} CaO$$

$$Ba(NO_3)_2 \xrightarrow{480°C} BaCO_3 \xrightarrow{750°C} BaO.$$

However, a further study using X-ray diffraction revealed that calcium and barium carbonates decomposed into oxides at a lower temperature in the presence of nickel, and in the case of calcium the decomposition was complete by about 550°C. Thus, the components effective for promo-

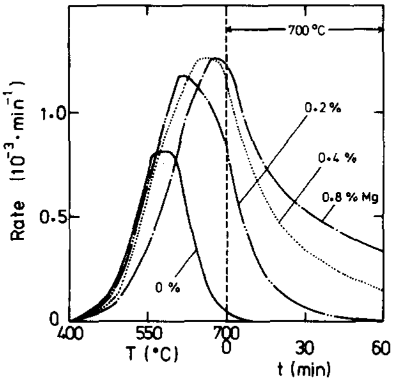

FIG. 6. Remaining reactivity of carbon with Ni-Mg catalysts at 700°C.

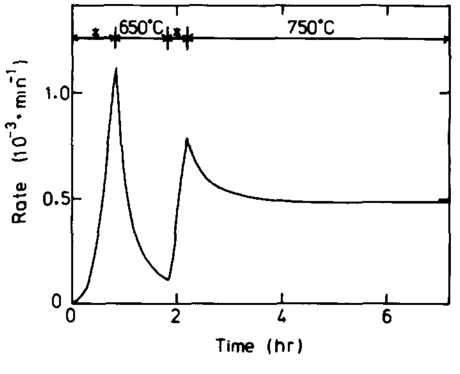

FIG. 7. Isothermal hydrogasification of carbon with Ni(5%)-Ca(1%) catalyst at 650 and 750°C. (*), Heating-up period at 5°C/min.

tion seem to be oxide for both LTR and HTR.

In the normal procedure, the carbon specimen was impregnated with the nickel and the promoter simultaneously. When the magnesium salt was loaded on carbon and decomposed at a temperature of between 400 and 900°C in advance of nickel impregnation, the reactivity of the specimen was nearly the same. But when the impregnation and reduction of nickel preceded the addition of magnesium salt, the conversion in LTR was about two-thirds of that of simultaneous impregnation (3.7 to 5.9%).

In preparing the nickel-calcium catalyst, acetate, hydroxide, or chloride of calcium was used instead of nitrate. The former two gave essentially the same reactivity, while chloride was ineffective and rather inhibited the reaction. It seems probable that those salts which yield an oxide upon thermal decomposition are the effective promoters. The inhibition by calcium chloride may be ascribed to the action of chlorine ions (*14*, *15*), as well as to the form of the decomposition product.

The dispersion of nickel was examined using X-ray diffraction line broadening (XD), scanning electron microscopy (SEM), and temperature-programmed desorption of hydrogen (TPD). The average diameter of nickel crystallites from XD and the percentage of dispersion from TPD are tabulated in Table 1, which shows that nickel crystallite was smaller in the presence of a promoter, especially of magnesium salt. SEM observation gave the same trend (Fig. 8). Thus the effect of promoters is, at least partly, associated with the increased dispersion of nickel.

TABLE 1

Dispersion of Nickel on Carbon[a]

| Heat-treatment temperature (°C) | Average crystallite diameter[b] (nm) | | | Dispersion[c] (%) | | |
|---|---|---|---|---|---|---|
| | Ni | Ni-Mg | Ni-Ca | Ni | Ni-Mg | Ni-Ca |
| 400 | 29 | 4 | 17 | 3.0 | 14.3 | 3.7 |
| 550 | 36 | 6 | 23 | 0.3 | 7.7 | 0.9 |
| 700 | 46 | 22 | 46 | 0.05 | 2.3 | 0.1 |
| 850 | 63 | 32 | 51 | — | — | — |

[a] Catalyst: Ni 5%, Mg or Ca 1%.

[b] From X-ray diffraction line broadening.

[c] Calculated from the amount of hydrogen desorbed in TPD.

## DISCUSSION

### *Mechanism of Gasification and the Effect of Promoters*

The mechanism of catalytic hydrogasification has been the subject of several studies, but no conclusive explanation has yet been given. Whether the catalyst excites the hydrogen or carbon is still a matter of debate (*16*). Without a fixed mechanism for the gasification, it is difficult to ascertain the role played by the promoters. The specific feature of promotion by the additives is that it causes the methane formation peak to shift to higher temperatures (Figs. 1–3). The decrease in the rate beyond the peak temperature can be explained by the sintering of nickel particles. If so, the promotion by the additives is ascribed to the suppression of sintering, so that a larger degree of three-phase contact (carbon–nickel–gaseous hydrogen) is maintained. Such a three-phase contact region may be directly associated with the gasification reaction. Alternatively, gasification may occur through hydrogen atoms spilled over from nickel to the carbon surface (*17*, *18*). In both cases, the correlation of nickel dispersion and the reactivity can easily be understood.

The role of alkaline earth oxides in nickel dispersion would be an anchoring action on the carbon surface, in which small nickel particles are stabilized. This needs a still more detailed explanation which can only be speculated upon here. Perhaps the promoters on the carbon surface are immobile and nickel atoms and minute particles attached to them become stable. Another study in this laboratory has revealed that nickel particles on carbon aggregate in a

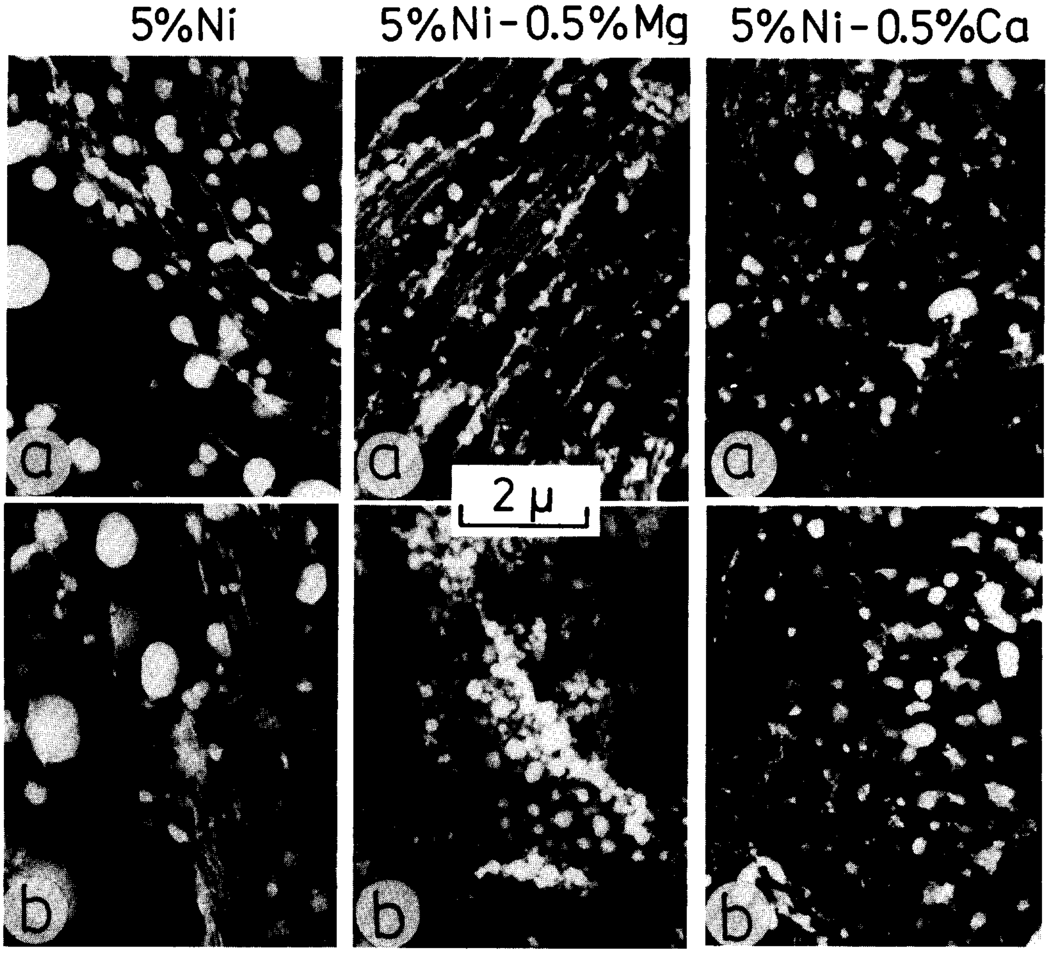

FIG. 8. SEM photographs of carbon gasified with Ni, Ni-Mg, and Ni-Ca catalyst. Different sections of an identical specimen are indicated by a and b.

manner similar to Ostwald ripening, i.e., particles do not move over the surface but larger particles grow in the dispense of smaller particles (*19*). The interaction between nickel and promoters is not clear. Before reduction, nickel oxide might partly form a compound or a solid solution with magnesia or alumina at the interface. Nickel aluminate is reported to be reduced only slightly at the temperature employed (*20*). These points need further study.

An important point to be mentioned is that promoters do not increase the intrinsic activity of nickel, rather decrease it. In other words, the turnover number, if this could be defined, would be smaller when the promoters were added. This can be seen in Figs. 2 and 3, when the rates of methane formation are compared at some lower temperature, say 550°C. Thus the promoting action for LTR seems to depend on the ability to suppress, or retard, the sintering.

### *Promotion of High-Temperature Reaction*

In the present study, only the calcium compounds enhanced the HTR. The better dispersion of nickel caused by the promoter might be favorable for the reaction, but the ability to keep dispersion was largest with magnesium, which failed to enhance the

HTR. One of the mechanisms suggested for HTR is that the carbon dissolves into the nickel and is gasified at another part of the nickel surface (*21–23*). In the case of graphite, nickel is reported to catalyze the C–$H_2$ reaction through the formation of channels (*24, 25*). Calcium may interact with carbon to facilitate the dissolution into nickel. Though the bulk of the promoter is estimated to be in an oxide form, this would not deny the possibility that the calcium closely attached to the nickel might be in a metallic form as a result of the action of hydrogen atoms supplied from the nickel. Metallic calcium seems to have a larger affinity to carbon than magnesium. This is inferred from the facts that calcium can intercalate graphite (*26*) and calcium carbide is stabler than magnesium carbide (*27*). In the present case, the hypothesis of strong interaction between carbon and the promoter is unnecessary, but we think that a situation similar to "incipient intercalation model" as suggested by Otto and Shelef (*28*) might occur at the time of gasification. Several studies have been done on the catalysis of calcium compounds for carbon gasification with steam, carbon dioxide, or oxygen, either as a direct catalyst (*29–33*) or as an assisting agent (*34–36*), but the promotion of hydrogasification has not yet been reported.

The decrease in methane formation in HTR with an increase in temperature seems to be associated with the thermodynamic equilibrium coupled with the pore diffusion problems. The conversion obtained in the present study was rather small. When gasification was conducted at elevated pressures, the conversion became quite high, and the promoters displayed their roles in a more distinct manner. The pressure dependence will be reported later.

## ACKNOWLEDGMENT

This work was supported by the Ministry of Education, Science, and Culture (Grand-in-Aid for Energy Research).

## REFERENCES

*1.* Johnson, J. L., *Catal. Rev.* **14,** 131 (1976).

*2.* Wigmans, T., and Moulijn, J. A., *in* "Proceedings 7th International Congress on Catalysis, Tokyo, 1980," Part A, p. 501. Kodansha, Tokyo, 1981.

*3.* Weber, J., and Bastick, M., *in* "Preprints, Carbon '76, 2nd International Carbon Conference, Baden-Baden, 1976," p. 120.

*4.* Tomita, A., and Tamai, Y., *J. Catal.* **27,** 293 (1972).

*5.* Nishiyama, Y., and Tamai, Y., *in* "Preprints, Division Fuel Chemistry, American Chemical Society, Honolulu, 1979," Vol. 24 (2), p. 219.

*6.* Tamai, Y., Nishiyama, Y., and Hagiwara, H., *Nippon Kagaku Kaishi* **1978,** 1670.

*7.* Inui, T., Funabiki, M., and Takegami, Y., *J. Chem. Soc. Faraday Trans. I* **76,** 2237 (1980).

*8.* Sinfelt, J. H., and Via, G. H., *J. Catal.* **56,** 1 (1979).

*9.* McVicker, G. B., Garten, R. L., and Baker, R. T. K., *J. Catal.* **54,** 129 (1978).

*10.* Ioffe, M. S., Kuznetsov, B. N., Ryndin, Yu. A., and Ermakov, Yu. I., *in* "Proceedings 6th International Congress on Catalysis 1976," Vol. 1, p. 131. 1977.

*11.* Lawson, J. D., and Rase, H. F., *Ind. Eng. Chem. Prod. Res. Dev.* **9,** 317 (1970).

*12.* Anderson, R. B., Hall, W. K., and Hofer, L. J. E., *J. Amer. Chem. Soc.* **70,** 2465 (1948).

*13.* Haga, T., and Nishiyama, Y., *Carbon,* in press.

*14.* Veraa, M. J., and Bell, A. T., *Fuel* **57,** 194 (1978).

*15.* Hedden, K., Kopper, H. H., and Schulze, V., *Z. Phys. Chem. (Frankfurt)* **22,** 23 (1959).

*16.* Holstein, W. L., and Boudart, M., *J. Catal.* **72,** 328 (1981).

*17.* Inui, T., Ueno, K., Funabiki, M., Suehiro, M., Sezume, T., and Takegami, Y., *J. Chem. Soc. Faraday Trans. I* **75,** 1495 (1979).

*18.* Rewick, R. T., Wentrcek, P. R., and Wise, H., *Fuel* **53,** 274 (1974).

*19.* Arai, M., Ishikawa, T., and Nishiyama, Y., *J. Phys. Chem.* **86,** 577 (1982).

*20.* Anderson, J. R., "Structure of Metallic Catalysts," p. 211. Academic Press, New York, 1975.

*21.* Wigmans, T., Elfring, M., Hoogland, A., and Moulijn, J. A., *in* "Proceedings International Conference of Coal Science, Düsseldorf, 1981," B19.

*22.* Hahn, R., and Hüttinger, K. J., *Chem.-Ing.-Tech.* **50,** 954 (1978).

*23.* Grigov'er, A. P., Lifshits, S. K., and Shamaes, P. P., *Kinet. Catal.* **18,** 948 (1977).

*24.* Keep, C. W., Terry, S., and Wells, M., *J. Catal.* **66,** 451 (1980).

*25.* Baker, R. T. K., and Sherwood, R. D., *J. Catal.* **70,** 198 (1981); Baker, R. T. K., Sherwood, R. D., and Derouane, E. G., *J. Catal.* **75,** 382 (1982).

*26.* Guerard, D., and Herold, A., *C. R. Acad. Sci. Ser. C* **280,** 729 (1975); *Carbon* **18,** 257 (1980).

*27.* Gmelin Handbuch, **27,** Tl.B, Lfg. 2, 299 (1939); **28,** Tl.B, Lfg. 3, 820 (1961).

*28.* Otto, K., and Shelef, M., *Carbon* **15,** 317 (1977).

*29.* Otto, K., Bartosiewicz, L., and Shelef, M., *Carbon* **17,** 351 (1979).

*30.* McKee, D. W., *Carbon* **17,** 419 (1979).

*31.* Cairns, J. A., Keep, C. W., Bishops, H. E., and Terry, S., *J. Catal.* **46,** 120 (1977).

*32.* Muralidhara, H. S., and Sears, J. T., *Chem. Eng. Prog. Coal Process Technol.* **4,** 22 (1978).

*33.* Hippo, E., and Walker, P. L., Jr., *Fuel* **54,** 245 (1975).

*34.* Sulima, A., Heek, K. H. van, and Jüntgen, H., *in* "Proceedings International Conference on Coal Science, Düsseldorf, 1981," B21.

*35.* Feldmann, H. F., Choi, P. S., Conkle, H. N., and Chauhan, S. P., *Chem. Eng. Prog. Coal Process Technol.* **5,** 205 (1979).

*36.* Forney, A. J., Haynes, W. P., and Gasior, S. T., *Energy Sources* **2,** 1 (1975).