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Disproportionation of CO on Ni/SiO_2: Kinetics and Nature of the Deposited Carbon

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The disproportionation of CO was studied at 275°C. The nature of the deposited carbon was determined using a low-field magnetic method. It was concluded that bulk nickel carbide was being formed. Moreover, a small amount of carbon was dissolved interstitially in the Ni lattice. Carbon deposited from methane on the same catalyst and at the same temperature behaved differently. In that case only a surface nickel carbide was being formed. The different behavior of carbon originating from CO and from carbon deposited from CH_4 is explained by the presence of oxygen on the Ni surface during the Boudouard reaction: a small fraction of the adsorbed oxygen atoms penetrates into the surface layer, thus bringing about a reconstruction of the surface. Owing to the reconstruction, carbon atoms can migrate more easily into the bulk of the Ni particles. The kinetics of the Boudouard reaction were also studied. Preliminary experiments showed that the rate-determining step is not the dissociation of CO, but the reaction of adsorbed oxygen with CO via a Langmuir–Hinshelwood mechanism. © 1985 Academic Press, Inc.

INTRODUCTION

The interaction of CO with nickel catalysts is an important step in the catalytic methanation reaction. It has been suggested (*1*, *2*) that CO is dissociatively chemisorbed, whereas other authors (*3*) state that molecularly adsorbed CO reacts with adsorbed hydrogen. Both dissociative adsorption and hydrogenation of molecularly adsorbed carbon monoxide lead to chemisorbed carbon. Several papers (*4*, *5*) deal with the reactivity of carbon deposited on nickel catalysts by the Boudouard reaction: $2CO \rightarrow C + CO_2$. However, minor attention has been paid to the chemical nature of the carbon deposit. Using "temperature-programmed surface reaction" McCarty and Wise (*5*) reported the existence of two distinct carbon species: an α-state was considered to represent isolated carbon atoms, while a β-state was thought to be amorphous carbon. Martin *et al.* (*6*) studied the Boudouard reaction using a high-field magnetic method. These authors interpreted their results, which were obtained at fairly small carbon contents, by assuming that the resulting carbon was interstitially dissolved in the Ni lattice.

The literature on the mechanism of the Boudouard reaction is conflicting. Araki and Ponec (*1*) and Van Ho and Harriot (*3*) agree that the rate-determining step is the dissociative adsorption of CO, which is followed by a rapid reaction between the resulting adsorbed oxygen and CO to yield CO_2. Biloen *et al.* (*7*), on the other hand, suggest that during the methanation, which generally proceeds faster that the Boudouard reaction (*3*), CO is rapidly dissociated, whereas the surface carbon thus obtained is hydrogenated slowly to methane.

This paper deals with the disproportionation of CO on a Ni/SiO_2 catalyst at 275°C. To elucidate the chemical nature of the carbon deposit we used a low-field magnetic method. The results obtained for carbon

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taken up by the catalyst from CO are compared with the results obtained for carbon from CH_4. In earlier work (*8–10*) we already reported on the deposition of carbon from CH_4. To allow a reliable comparison we decomposed CH_4 on the same catalyst and at the same temperature as employed for the disproportionation of CO.

In order to establish the rate-determining step in the disproportionation of CO we compared the rate of the Boudouard reaction with the rate of the reaction between CO and preadsorbed oxygen both at 275°C.

EXPERIMENTAL

The carbon monoxide of high purity (99.997%) used in the study of the Boudouard reaction was delivered by L'Air Liquide Belge. Hydrogen used in the adsorption experiments was purified by diffusion through palladium. The decomposition of CH_4 was studied with a mixture of 10.2% CH_4 in N_2 (impurities less than 70 ppm), delivered by Matheson.

The catalyst previously denoted by U_{42} (*8, 9*) was prepared by the method of homogeneous deposition-precipitation, as described elsewhere (*11, 12*). The specific surface area of the silica used (Aerosil, Degussa) was 380 m^2 g^{-1}. The loaded carrier (50 wt% Ni) was dried at 120°C, pressed and cut into small bodies of dimensions between 1.5 and 2.5 mm. Reduction was carried out at 450°C in a flow of 10% H_2 in Ar for at least 80 hr. After reduction the sample was evacuated for 5 hr at 425°C. The specific nickel surface area of the catalyst was determined by means of hydrogen chemisorption at 30°C, and found to be 90 m^2 (g Ni)$^{-1}$ (0.28 ml STP H_2/m^2 Ni). The particle size distribution of catalyst U_{42} was obtained by means of a vibrating sample magnetometer (fields up to 14 kOe), which has been described before (*8*).

The Boudouard reaction was studied in the Pyrex high-vacuum system also described previously (*8*). In the same apparatus the chemisorption of hydrogen was investigated. During the interaction with CO (or H_2) the magnetization of the catalyst sample was measured in a low-field apparatus (H = 66 Oe; 1 Oe = 79.58 A m^{-1}), details of which have been given by Erkelens and Wösten (*13*); the accuracy of the magnetization measurements is about 1%.

The pulse-flow experiment on the decomposition of methane was carried out with the catalyst in the measuring cell of the vacuum equipment. The cell was connected to the flow apparatus set out in detail in earlier work (*9*). Gas leaving the catalyst bed was led directly (without passing through a separation column) into the analysis system of a Perkin–Elmer F17 gas chromatograph, which was equipped with a flame ionization detector. The extent of decomposition of a methane dose could be established very accurately by comparing the detector response for the methane in the product gas with the response obtained when a methane pulse was introduced into the detector via a bypass, thus avoiding the passage through the reactor. After carbon deposition the sample cell was transferred to the low-field magnetic equipment and the magnetization was measured.

RESULTS

Boudouard Reaction

The disproportionation of CO at 275°C was studied on a reduced and evacuated sample of catalyst U_{42} containing 0.76 g Ni. After admission of a CO dose the total pressure was recorded continuously. The CO_2 evolved was condensed in a cold trap kept at 77 K. It was observed that a small fraction of the admitted CO adsorbed instantaneously. The fast adsorption was followed by a more gradual and linear drop of the pressure. After the pressure had decreased to less than 0.2% of the initial value, the catalyst was evacuated until a vacuum of 10^{-5} Torr (1 Torr = 133.3 N m^{-2}) was reached. The catalyst was next cooled down to 30°C and its magnetization was measured. Subsequently the sample cell was isolated from the system and the cold trap, containing the solid CO_2, was brought to room temperature. From the amount of gaseous CO_2 evolved, generally equal to 47 ± 2% of the CO disappeared, the amount of carbon deposited on the catalyst according to the equation $2CO \rightarrow C + CO_2$ was determined. This procedure was repeated for each CO dose.

To study the effect of the volume of the CO dose four different "isotherms" have been measured, which differed in the average size of the admitted CO doses. Each isotherm was obtained by admitting a sequence of CO doses to the catalyst sample. After each dose the procedure described above was followed. The average CO dose in the four isotherms was 2.8, 6.0, 10.8, and 17.8 ml STP (g Ni)$^{-1}$, respectively. Between successive CO isotherms the deposited carbon was removed from the catalyst by reaction with flowing hydrogen at 300°C for 5 hr. This treatment was followed by a reduction at 450°C in a flow of 10% H_2 in Ar for about 80 hr. After subsequent evacuation the magnetization displayed its initial value, which indicated a complete removal of the carbon.

Figure 1 shows the four CO isotherms; in this figure M_0 is the magnetization of the freshly reduced and evacuated catalyst and M is the actual magnetization. The measurement of each isotherm was ended arbitrarily before the uptake of carbon and the corresponding decrease of the magnetization had come to saturation. In Fig. 2 the magnetization–volume isotherm for hydrogen adsorption at 30°C on the same catalyst sample is shown. Whereas the disproportionation of CO causes the magnetization to drop to very low values, the adsorption of hydrogen reduces the relative magnetization at most by 26% (final hydrogen pressure 250 Torr).

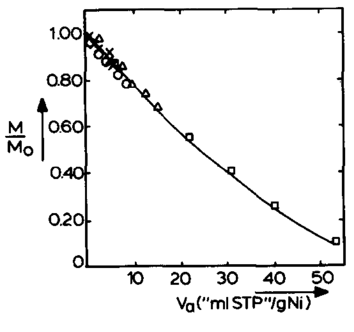

FIG. 1. The decrease of the relative magnetization as a function of the amount (V_a) of carbon adsorbed during the Boudouard reaction. V_a is expressed as the amount of CO_2 evolved; (×) average CO dose of 2.8 ml (g Ni)$^{-1}$, (○) average CO dose of 6.0 ml (g Ni)$^{-1}$, (△) average CO dose of 10.8 ml (g Ni)$^{-1}$, (□) average CO dose of 17.8 ml (g Ni)$^{-1}$.

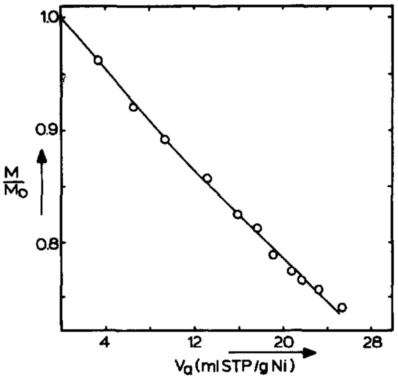

FIG. 2. The magnetization–volume isotherm for hydrogen adsorption at 30°C.

From Fig. 1 it can be seen that the maximum uptake of carbon attained in our experiments is about 53 "ml STP" of carbon per gram nickel. This number can be related to the monolayer coverage as determined by hydrogen adsorption. The maximum uptake of H_2 at 30°C and 250 Torr amounted to 25 ml STP (g Ni)$^{-1}$. Knowing that hydrogen is dissociatively chemisorbed and that each molecule occupies two nickel sites upon chemisorption, the carbon surface coverage can be calculated provided the bond number of carbon is known. From earlier work (*8*) it is known that a surface carbon atom deposited from CH_4 occupies 3 nickel atoms. Hence, a monolayer of surface carbon would correspond to $\frac{1}{3} \times (25 \times 2) = 16.7$ "ml STP" C (g Ni)$^{-1}$. The maximum uptake of carbon in our experiments therefore corresponds to $53/16.7 = 3.2$ monolayers. During the experiment with the largest CO doses (17.8 ml STP (g Ni)$^{-1}$), also kinetic measurements have been carried out. After admission of the first dose the CO pressure was observed to drop linearly with time. In Table 1 the rate of decrease of the CO pressure at different times and CO pressures is shown. With subsequent doses the pressure continued to decrease linearly. The rate of decrease is represented in Table 2 as a function of the amount of carbon deposited, C_{dep}.

Carbon Deposition from CH_4

To compare the nature of the carbon deposited from CH_4 and from CO the following (flow)experiment was carried out. For 95 hr pulses of 0.13 ml STP of methane (1.25 ml of 10.2 vol% CH_4 in N_2) were dosed every 12.5 min into a nitrogen flow (50 cm^3 min^{-1}), which passed through a sample (Ni content 0.71 g) of catalyst U_{42} kept at 275°C. The catalyst had been previously reduced at 450°C in a flow of 10% H_2 in Ar (same procedure as above) and subsequently freed from adsorbed hydrogen in a flow of nitrogen also at 450°C. The first 20 pulses of methane were taken up completely. After 75 pulses an apparently steady state was reached in which about 48% of each methane dose was decomposed. At the end of the experiment the catalyst had taken up an amount of carbon corresponding to 44.2 ml STP CH_4 (g $Ni)^{-1}$. The relative magnetization of the catalyst had dropped to a value of 0.69 ± 0.02.

Interaction of CO and H_2 with Preadsorbed Oxygen

In the literature the reaction between oxygen adsorbed on Ni surfaces and carbon monoxide has often been proposed to be a fast step (*1*, *3*). In order to verify this we carried out the following experiment: 17.9 ml STP of O_2 was admitted to a reduced and evacuated sample of catalyst U_{42} containing 0.63 g Ni, which was kept at 30°C. The oxygen was taken up completely. During this treatment the magnetization of the sample decreased by 27%. After evacuation at 275°C 40 Torr of CO was admitted to the catalyst also at 275°C. The CO_2 evolved was condensed in a cold trap kept at 77 K. After 60 min the remaining CO was pumped off, the connection between the dosing system and the sample cell was closed, and the cold trap was heated up to room temperature. The CO_2 pressure measured when the trap was at room temperature revealed a mean rate of CO_2 production of 1.3 ml STP (g $Ni)^{-1}$ hr^{-1}. During the reaction of CO with the preadsorbed oxygen the relative magnetization of the catalyst sample rose from 73 to 77%. The above experiment was repeated under the same experimental conditions (temperature, pressure) with H_2 instead of CO. After a decrease of the magnetization by 27% due to the chemisorption of O_2, reaction between H_2 and O(ads) for 60 min raised the magnetization to 93% of its original value. The increase in magnetization during reaction with H_2 was hence larger than with CO. We therefore conclude that at a pressure of 40 Torr the reaction between O(ads) and H_2 is much faster than the reaction between O(ads) and CO. However, it was observed that the rate of the latter reaction depends on the surface cov-

TABLE 1

Rate of the Boudouard Reaction after Admission of the First CO Dose

Time (hr)	CO pressure (Torr)	Conversion rate (ml STP CO/g Ni hr)
0	6.6	2.98
1	5.1	2.96
2	3.7	2.91

TABLE 2

Rate of the Boudouard Reaction as a Function of the Amount of Carbon Deposited, C_{dep}

C_{dep} ("ml STP" C/g Ni)	Conversion rate (ml STP CO/g Ni hr)
0	2.98
12.2	2.79
22.1	2.48

erage of oxygen. After chemisorption of 13.1 ml STP of O_2 (instead of the above 17.9 ml) the mean rate of CO_2 production during the admission of 12 CO doses (of 2.9 Torr each) was slightly higher, viz., 1.9 ml CO_2 (g Ni)$^{-1}$ hr^{-1}. It could be argued that during the reaction of CO with O(ads) also the Boudouard reaction proceeds. As was shown above, this would result in an hourly production of 1.5 "ml STP" C at most, resulting in a decrease of the relative magnetization by about 2.5% (see Fig. 1). The overall magnetic effect being an increase by 4% could then be considered as the result of a decrease by 2.5% due to carbon deposition and an increase by 6.5% due to the removal of surface oxygen. This increase by 6.5%, however, is still much smaller than the increase by 20% observed during the reaction of O(ads) with H_2. Hence, we can sustain our conclusion that H_2 reacts much faster with preadsorbed oxygen than CO does. We feel, moreover, that the experimental data provide evidence that the Boudouard reaction hardly proceeds during the reaction of CO with O(ads). From the magnetic results it can be derived that in that case the amount of CO_2 produced should have been much larger than actually was measured. In our opinion the disproportionation of CO is strongly retarded due to the presence of the large oxygen surface coverage of about 1.1 monolayer (or 0.8 monolayer in the second experiment), which suppresses the dissociation of CO requiring free nickel sites.

DISCUSSION

From the results of Table 1 it can be seen that the steady-state rate of the Boudouard reaction depends hardly at all on the CO pressure. The rate of the reaction is hence determined mainly by the number of active sites on the Ni surface. Table 2 shows that the rate of the reaction, and according to the above also the number of active sites, varies only slightly with the amount of carbon deposited. At 275°C the deposited carbon apparently does not markedly deactivate the catalyst.

The lack of deactivation may be due to diffusion of carbon atoms into the nickel particles and/or to formation of filamentous carbon between the nickel particles and the support. Rostrup-Nielsen (*14*), Tøttrup (*15*) and Gardner and Bartholomew (*16*) established electron microscopically the formation of carbon filaments on top of which a nickel particle was attached. While Tøttrup and Gardner and Bartholomew observed the formation of carbon filaments at 280 to 425°C, Rostrup-Nielsen found the filaments at much more elevated temperatures, viz., 450–700°C. When carbon filaments are thus formed, the free Ni surface area hardly changes. Schouten *et al.* (*17*) observed that carbon deposited from CH_4 onto a Ni (110) surface diffused into the bulk at temperatures above 300°C.

Our magnetic results indicate that in our experiments carbon migrated into the nickel particles. Growth of carbon filaments out of the Ni particles cannot be expected to affect the ferromagnetism of the catalysts as drastically as is apparent from Fig. 1. Interaction with CO caused the relative magnetization to drop to 0.10, whereas a catalyst fully covered by hydrogen (hydrogen pressure 250 Torr) showed a relative magnetization of 0.74. Disproportionation of carbon monoxide consequently not only affects the magnetic moments of the nickel surface atoms, but also those of bulk atoms. Carbon atoms must therefore have penetrated into the bulk.

In an earlier work (*8, 10*) we reported on the nature of the carbon deposited on different Ni/SiO$_2$ catalysts from CH_4. Isothermal chemisorption of CH_4 at 100°C by catalyst U_{42} led to formation of a surface nickel carbide, according to: $CH_4 + 7Ni \rightarrow Ni_3C + 4Ni\text{–}H$.

In an experiment where methane reacted with Ni/SiO$_2$ particles as temperatures gradually increasing from 30 to 300°C, surface nickel carbide was also formed. At more elevated surface coverages obtained at the higher temperatures CH_x adsorption complexes not affecting the ferromagnetism were found.

It is remarkable that the reaction with methane, though leading to a surface nickel carbide, does not give rise to migration of carbon atoms into the nickel particles as was observed during the reaction with carbon monoxide. Even with amounts of deposited carbon larger than required to convert the surface completely into nickel carbide, no evidence for migration into the bulk was found. To establish the difference more accurately the pulse-flow experiment dealt with in the previous section was carried out. In this experiment methane was decomposed at the same temperature as during the disproportionation of CO. 44.2 ml STP (g Ni)$^{-1}$ of methane was decomposed at 275°C; after the reaction the relative magnetization still amounted to 0.69 ± 0.02. The uptake of an equal amount of carbon from CO at 275°C decreased the relative magnetization to 0.18 ± 0.02 (Fig. 1).

Higher coverages of carbon deposited from CO therefore affect the ferromagnetism more than carbon from methane. The formation of nickel carbide during the decomposition of methane is confined to the surface layer of the nickel particles, whereas carbon penetrates into the nickel when it has been deposited from carbon monoxide in this work, viz., 53 ml STP of carbon in bulk nickel at 275°C is very small, viz., less than 0.1 at.% (*18*). The largest amount of carbon deposited from carbon monozide in this work, viz., 53 ml STP of carbon (g Ni)$^{-1}$, corresponds to not less than 14 at.%, and hence appreciably exceeds the equilibrium solubility. As this amount of carbon rendered the nickel particles almost completely nonferromagnetic, the carbon must have been dissolved substantially into the nickel. To investigate the nature of the solid solution, we will consider the magnetic results more quantitatively.

The number of Ni atoms transferred to a nonferromagnetic state per carbon atom taken up can in principle be determined by comparing the magnetic effect of equal volumes of adsorbed CO and H_2. Measurements of the saturation magnetization have shown that adsorption of a hydrogen molecule leads to a loss of the contribution of about 2 Ni atoms to the collective magnetization of a nickel particle (*19*). A reliable calculation of the magnetic effect per atom taken up from a comparison of the initial slopes of low-field magnetization-volume isotherms calls, however, for an equal distribution of the adsorbed or deposited atoms over the differently sized Ni particles of the catalyst (*8*). As this will not be the general case, the most reliable bond number is obtained by comparing the magnetic effects at adsorption of a monolayer. However, this is possible only if the monolayer coverage of the gas molecules, the magnetic effect of which has to be determined, can be assessed sufficiently accurately. Since the interaction with CO does not exhibit a marked discontinuity at a monolayer coverage, this procedure cannot be applied.

We therefore calculated the bond number from the ratio of the slopes of the magnetization–volume isotherms for carbon monoxide and hydrogen. The ratio leads to a bond number of 4.2 ± 0.3, which would indicate annihilation of the contribution of about 4 Ni atoms to the ferromagnetism by the uptake of one carbon atom from CO. Since the slope of the isotherm measured with CO does not vary with the size of the CO dose, the rate of transport of CO molecules at 275°C through the pores of the catalyst was not strongly affecting the distribution over the Ni particles. Hence, there is an almost uniform coverage of chemisorbed carbon atoms over all nickel particles. When, however, the distribution of carbon monoxide and hydrogen over the nickel particles of varying size is unequal, the bond number calculated above has a much smaller accuracy than is suggested by the experimental accuracies of the slopes. In earlier work (*10*) the evidence pointed to an initial preferential adsorption of hydrogen onto the larger Ni particles which are likely to be present in wide pores. The distribution of CO is therefore more uniform than that of hydrogen. Consequently, the above value of 4.2 has to be considered as a lower limit.

Martin *et al.* (*6*) studied the Boudouard reaction using a high-field magnetic method. These authors carried out the reaction differently. They adsorbed CO at room temperature and subsequently raised the temperature stepwise to 700 K at which temperature the CO dosed had completely reacted. From the measurement of the saturation magnetization, which is not affected by the distribution over the Ni particles provided the magnetic effect per carbon atom does not depend on the Ni particle size, they arrived at a number of 6 to 5 Ni atoms becoming nonferromagnetic by accommodation of one carbon atom. They noted a tendency of this number to decrease with increasing uptake of carbon. The difference with our experiments is that Martin *et al.* started with an amount of CO leading to a final carbon content of at most 4 at.%, whereas in our work a final content of about 14 at.% was reached. As indicated by the single-crystal experiments of Schouten *et al.* (*17*), carbon can dissolve in Ni without formation of a stoichiometric carbide. Schouten *et al.* observed the dissolution of carbon to start at 300°C, while Martin *et al.* used a final temperature of 425°C. Hence, formation of an interstitial solution could proceed in the experiments of Martin *et al.* The evidence, which is supported by work on bulk Ni (*20*), points to annihilation of the contribution of about 6 Ni atoms by one carbon atom. At higher loadings with carbon, Ni_3C is obtained and as a result the bond number drops. It is obvious that at the higher loading with carbon used in our experiments more Ni_3C is formed and that the mean bond number is consequently lower.

We feel that the solubility that was found in this work being much higher than that observed with bulk Ni is due to the difficult nucleation of graphite, the stable modification of carbon. As no graphite can nucleate, the carbon atoms dissolve in the nickel rather than remain in an amorphous state on the surface.

The rate of disporportionation of CO (Tables 1 and 2) was found to be about 2.9 to 2.5 ml STP CO (g Ni)$^{-1}$ hr^{-1}, corresponding with the production of 1.45 to 1.25 ml STP CO_2 (g Ni)$^{-1}$ hr^{-1}. Moreover, a nearly zero order with respect to the CO pressure was observed. In the experiments on the reactivity of preadsorbed oxygen toward CO the rate of the CO_2 production, respectively 1.3 and 1.9 ml STP (g Ni)$^{-1}$ hr^{-1}, was of the same order of magnitude as the rate of the Boudouard reaction. The experimental reaction rates therefore indicate that the rate-determining step in the disproportionation of CO is the reaction of O(ads) with CO rather than the dissociation of CO. Moreover, because the kinetic measurements were performed at extremely small surface coverages of carbon (see Table 1), the diffusion of adsorbed carbon into the bulk of the nickel particles can be eliminated as a possible slow step. To reconcile the proposed mechanism with the observed zero order with respect to the CO pressure, it has to be assumed that the rate-determining step proceeds via a Langmuir–Hinshelwood mechanism. Hence, the reaction sequence is as follows:

$$\mathrm{CO(g)} \rightleftarrows \mathrm{CO(ads)} \qquad \text{fast}$$

$$\mathrm{CO(ads)} \rightleftarrows \mathrm{C(ads)} + \mathrm{O(ads)} \qquad \text{fast}$$

$$\mathrm{CO(ads)} + \mathrm{O(ads)} \rightarrow \mathrm{CO_2} \qquad \text{slow}$$

At a pressure of 40 Torr the reaction of preadsorbed oxygen with H_2 was established to be much more rapid than the reaction between preadsorbed oxygen and CO. The reaction scheme shown therefore agrees with that proposed by Martin *et al.* (*6*) and by Biloen *et al.* (*7*). The latter authors concluded that in the Fischer–Tropsch reaction the rate-determining step is the hydrogenation of a CH_x species, which is generated on the surface by the rapid dissociation of CO. This explains why in the methanation reaction on Ni besides methane H_2O is the most abundant product, whereas CO_2 is produced only to a slight extent or not at all.

Though the agreement of the above rates of CO disproportionation and of the reaction of O(ads) with CO is striking, the reactivity of oxygen present on a nickel surface may vary considerably. Hence the reactivity of oxygen adsorbed from CO dissociated at 275°C may be different from that of oxygen adsorbed from O_2 at 30°C. We are now investigating the reactivity of oxygen adsorbed on Ni surfaces more closely.

We return finally to the question as to what leads to the observed difference in the deposition of carbon from CO and CH_4. As stated above, the Boudouard reaction proceeds via the dissociative adsorption of CO. Whereas with methane a surface carbide or perhaps a surface "hydride carbide" results, decomposition of carbon monoxide leads to a surface oxycarbide. The larger reactivity of oxygen causes the surface layer to be more severely distorted. Owing to the distortion carbon atoms may be able to penetrate into the bulk of the nickel particles. Though most of the oxygen ends up in the gaseous carbon dioxide, the small experimental deviation from complete reaction to CO_2 indicates a small fraction of oxygen remaining in the surface. This oxygen would hence "catalyze" the formation of bulk nickel carbide. When no oxygen at all is present on (or in) the surface, as in the decomposition of methane, the penetration of carbon is not catalyzed and the formation of nickel carbide is confined to the surface layer.

REFERENCES

1. Araki, M., and Ponec, V., *J. Catal.* **44,** 439 (1976).
2. Wentrcek, P. R., Wood, B. J., and Wise, H., *J. Catal.* **43,** 363 (1976).
3. Van Ho, S., and Harriot, P., *J. Catal.* **64,** 272 (1980).
4. Rabo, J. A., Risch, A. P., and Poutsma, M. L., *J. Catal.* **53,** 295 (1978).
5. McCarty, J. G., and Wise, H., *J. Catal.* **57,** 406 (1979).
6. Martin, G. H., Primet, M., and Dalmon, J. A., *J. Catal.* **53,** 321 (1978).
7. Biloen, P., Helle, J. N., and Sachtler, W. M. H., *J. Catal.* **58,** 95 (1979).
8. Kuijpers, E. G. M., Breedijk, A. K., Van der Wal, W. J. J., and Geus, J. W., *J. Catal.* **72,** 210 (1981).
9. Kuijpers, E. G. M., Jansen, J. W., Van Dillen, A.J., and Geus, J. W., *J. Catal.* **72,** 75 (1981).
10. Kuijpers, E. G. M., Breedijk, A. K., Van der Wal, W. J. J., and Geus, J. W., *J. Catal.* **81,** 429 (1983).
11. Van Dillen, A. J., Geus, J. W., Hermans, L. A. M., and van der Meijden, J., "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 2, p. 677. The Chemical Society, London, 1977.
12. Hermans, L. A. M., and Geus, J. W., *in* "Studies of Surface Science and Catalysis" (B. Delmon, P. Grange, P. Jacobs, and G. Poncelet, Eds.), Vol. 3, p. 113. Elsevier, Amsterdam, 1979.
13. Erkelens, J., and Wösten, W. J., *J. Catal.* **54,** 143 (1978).
14. Rostrup-Nielsen, J. R., *J. Catal.* **27,** 343 (1972).
15. Tøttrup, P. B., *J. Catal.* **42,** 29 (1976).
16. Gardner, D. C., and Bartholomew, C. H., *Ind. Eng. Chem. Prod. Res. Dev.* **20,** 80 (1981).
17. Schouten, F. C., Kaleveld, E. W., and Bootsma, G. A., *Surf. Sci.* **63,** 460 (1977).
18. Eizenberg, M., and Blakely, J. M., *Surf. Sci.* **82,** 228 (1979).
19. Martin, G. A., and Imelik, B., *Surf. Sci.* **42,** 157 (1974).
20. Cadeville, M. C., Gautier, F., and Robert, C., "Proceedings, 13th International Conference on Low Temperature Physics," Vol. 4, p. 325. Plenum Publishing Company, London, 1972.