JOURNAL OF CATALYSIS 6, 308–313 (1966)

# Reaction of Nickel with Carbon Monoxide at Elevated Temperatures

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Received March 23, 1966; revised June 23, 1966

The reaction of sheet nickel with carbon monoxide has been examined over the temperature range 300–650°C with a tracer apparatus employing $C^{14}$-labeled carbon monoxide. Evidence has been produced that the main reaction at all temperatures was the catalytic disproportionation of carbon monoxide upon the nickel surface, i.e., $2\ CO \rightarrow C + CO_2$ with direct reaction between nickel and carbon monoxide playing a minor, even negligible, role. The disproportionation reaction takes place readily upon abraded nickel surfaces but only with great difficulty upon electropolished surfaces. Possible explanations are suggested.

The reaction of nickel with carbon monoxide has received considerable attention hitherto, but almost invariably the metal has been in powder form, often dispersed upon some inert support such as kieselguhr. It was therefore considered that a further study with the nickel in sheet form, should provide valuable data. The techniques selected were designed to yield information regarding the deposition of carbon.

*A priori* the most likely reaction of nickel with carbon monoxide is

$$Ni + CO \rightarrow NiO + C$$

which, as the thermodynamic data show (Table 1) is favored by low temperature: The equilibrium pressure of carbon monoxide becomes equal to the pressure of reactant gas used in the present study (viz. 10 mm Hg) at 325°. Thermodynamic calculations show that the quantities of $Ni_3C$, $NiCO_3$, and $Ni(CO)_4$ formed at the temperatures and pressures in question would be zero or negligible, whereas the formation of carbon by disproportionation of carbon monoxide is thermodynamically feasible, as will be clear from Table 2.

TABLE 1

THERMODYNAMIC DATA FOR REACTIONS OF NICKEL WITH CARBON MONOXIDE[a]

$\Delta G^\circ_T = A + BT$

| Reaction: | $Ni + CO = NiO + C$ |
|---|---|
| $A$ (kcal mole$^{-1}$) | −31.75 |
| $B$ (kcal mole$^{-10}$ K$^{-1}$) | 0.0445 |
| $\Delta G^\circ_{600°K}$ (kcal mole$^{-1}$) | −5.05 |
| $\Delta G^\circ_{900°K}$ (kcal mole$^{-1}$) | +8.30 |
| $P_{CO}$ (600°K)[b] | 1.1 cm Hg |
| $P_{CO}$ (900°K)[b] | 104 atm |

[a] Reference (*1*).

[b] $P_{CO}$, equilibrium pressure of CO.

TABLE 2

THERMODYNAMIC DATA FOR THE REACTION[a] $2CO = C + CO_2$

$\Delta G^\circ_T = -40.80 + 0.0417T$ kcal mole$^{-1}$

| Temperature (°K) | $\Delta G^\circ_T$ | $K_P$ | $\alpha$[b] |
|---|---|---|---|
| 600 | −15.78 | $5.61 \times 10^5$ | 0.99 |
| 700 | −11.61 | $4.22 \times 10^3$ | 0.91 |
| 800 | −7.44 | $1.08 \times 10^2$ | 0.55 |
| 900 | −3.27 | 6.23 | 0.125 |
| 923 | −2.31 | 3.53 | 0.08 |

[a] Reference (*1*).

[b] $\alpha$ is the fraction of CO molecules which have undergone disproportionation. The minimum value of $\alpha$ detectable by the tracer technique was $\alpha = 0.01$.

## METHODS

**a. Materials.** Two different batches of nickel were used: (i) sheet nickel, 0.02 inch thick, of spectroscopically standardized grade (Johnson, Matthey, and Co., Ltd.), designated henceforth as "pure" nickel. Spectrographic analysis gave (ppm): Cu, 10; Si, 10; Al, 5; Ca, 3; Mg, 3; Ag, 1; and Mn, <1; (ii) sheet nickel 0.04 inch thick, (Henry Wiggin and Co., Ltd.), designated henceforth as "impure" nickel. Spectrographic analysis gave (ppm): Mg, 800; Fe, 500; Si, 200; Cu, 100; Al, 50; Mn, 20; Pb, 2; Ca, 1; and Ag, <1. By chemical analysis the carbon content of (i) was 20 ppm and of (ii) 320 ppm.

The samples (1.00 × 0.50 inch) were cut from the sheet and a hole (1/16-inch diameter) drilled in the face near to one end of each, to facilitate suspension in the reaction chamber. They were abraded on a metallurgical polishing wheel using 0 grade emery paper under a stream of petroleum ether (b.p. 100–120°C) and finished on 00 grade emery paper after turning through 90°. Finally they were degreased by suspension in a benzene still for 1 hr and were then immediately placed in the tracer apparatus, which was then sealed and evacuated.

Some of the samples after abrasion were further treated by electropolishing, using nickel cathodes and an electrolyte bath of dilute sulfuric acid (*2*), the current being passed for 3–5 min at a current density of 0.4 amp cm$^{-2}$. These samples, which displayed good optical reflectivity, were then removed from the bath and rinsed, first in water and then in acetone, before being placed in the tracer apparatus.

The C$^{14}$-labeled carbon monoxide was prepared by diluting a 1-mc sample of the highly active gas (from the Radiochemical Centre, Amersham) with four 1-liter bulbs of inactive, spectroscopically standardized carbon monoxide (British Oxygen Gases, Wembley). The specific activity of the gas thus became 0.25 $\mu$c cm$^{-3}$ at NTP; at 10 mm Hg pressure it gave a count rate of approximately 60 counts/sec on the Geiger-Muller tubes used in the tracer apparatus.

**b. Apparatus.** The tracer apparatus (*3*) (Fig. 1) consisted essentially of a reaction chamber A made of silica and 100 cm$^3$ in capacity, a counting cell C to the end of which was sealed a Geiger-Muller tube B (special end-window type EW3h, supplied by Twentieth Century Electronics, Ltd.), a Y-tube E, a mercury cutoff F and a calibrated bulb G. The reaction vessel, which was surrounded by a concentric furnace N, was connected by a Pyrex-silica graded seal to the main part of the apparatus; this was formed into a cyclic loop, small-bore connecting tubes being used in order

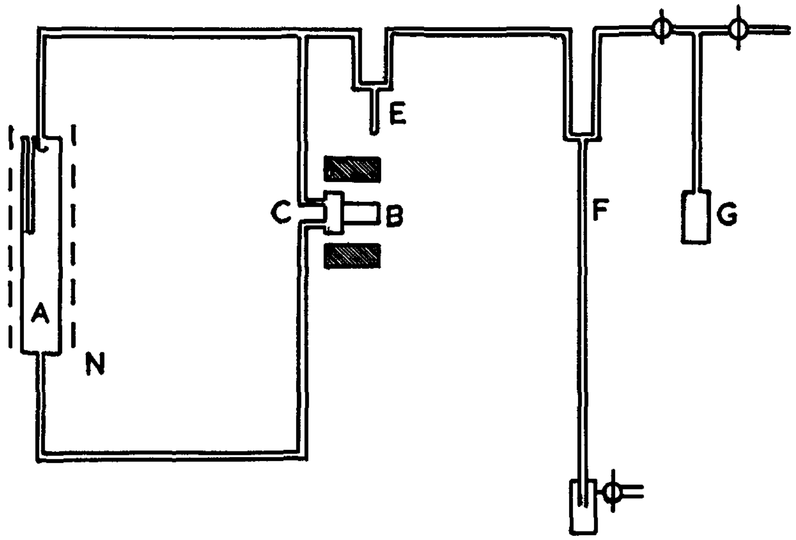

FIG. 1. The tracer apparatus: A, reaction chamber; B, Geiger-Muller counter; C, counting cell; E, cold finger; F, mercury cutoff; G, calibrated volume; N, furnace.

to restrict the total volume to approximately 150 cm$^3$.

With this apparatus a change in pressure of 0.1 mm Hg (the minimum detectable) was equivalent to an uptake of 9 $\mu$g of carbon by the specimen, corresponding to approximately 1.5 $\mu$g cm$^{-2}$. Loss of activity from the gas phase was assumed to denote deposition of carbon on the metallic specimen. Confirmatory evidence of this was obtained by (a) autoradiography, using Kodirex film, and (b) direct counting on the samples after reaction, using a Geiger-Muller counter with an end window. This latter auxiliary technique was of higher sensitivity than that based on loss of activity from the gas phase although it provided only qualitative evidence of carbon deposition.

## RESULTS

The experimental results are recorded in Table 3 for the four different modes of surface preparation. The correlation of the extent of reaction with (a) the presence of impurities and (b) surface damage, is

TABLE 3

DEPOSITION OF CARBON ON SHEET NICKEL EXPOSED TO CARBON MONOXIDE[a]

| | (i) Pure Nickel | | | | (ii) Impure Nickel | | | |
|---|---|---|---|---|---|---|---|---|
| | Abraded, then electropolished | | Abraded | | Abraded, then electropolished | | Abraded | |
| Temperature (°C) | Experiment No. | Result | Experiment No. | Result | Experiment No. | Result | Experiment No. | Result |
| 300 | 1 | 0 | 18 | + | 27 | 0 | 16 | + |
| | | | 30 | + | | | 42 | + |
| 310 | — | — | — | — | — | — | 22 | + |
| 330 | — | — | 19 | ++ | 28 | 0 | — | — |
| | | | 29 | ++ | | | | |
| 350 | 2 | 0 | 11 | ++[b] | 26 | 0 | 43 | + |
| | | | | | | | 45 | +[c] |
| | | | | | | | 46 | ++[c] |
| 360 | 8 | 0[b] | — | — | — | — | 13 | ++ |
| | | | | | | | 24 | ++ |
| | | | | | | | 48 | ++[c] |
| 390 | — | — | 10 | 0[b] | — | — | 12 | + |
| 400 | 3 | 0 | 20 | 0 | 25 | 0 | 14 | ++ |
| | 9 | 0[b] | 31 | 0 | | | 23 | ++ |
| | | | | | | | 49 | ++[c] |
| 420 | — | — | — | — | — | — | 17 | ++ |
| | | | | | | | 21 | ++ |
| 450 | 4 | 0 | — | — | — | — | 50 | ++[c] |
| 500 | 5 | 0 | — | — | — | — | | |
| 550 | 6 | 0 | 36 | 0 | 34 | + | 40 | ++[c] |
| | | | | | | | 32 | ++[c] |
| | 51 | 0[d] | | | | | 41 | ++[c] |
| | 39 | 0[e] | | | | | | |
| 600 | 7 | 0 | — | — | — | — | — | — |
| 650 | 38 | 0[e] | 37 | ++ | 35 | ++ | 33 | ++ |

[a] 0, no change in vapor-phase count rate and no measurable direct count rate; +, no change in vapor-phase count rate but a detectable increase in direct count rate; ++, significant change in vapor-phase count rate and large increase in direct count rate.

[b] Sample reduced *in situ* with hydrogen before reaction.

[c] Presence of $CO_2$ detected in gas phase. N.B. $CO_2$ formation was not specifically looked for in experiments before Number 40.

[d] Surface of nickel sample scratched with diamond before exposure to CO.

[e] Carbon had been deposited on the nickel by a shadowing technique before exposure to CO.

clear: The pure nickel after electropolishing gave no deposition of carbon at any of the temperatures investigated, even when it had been scratched with diamond, or when carbon had been previously deposited on it (by a shadowing technique as in electron microscopy); at the other extreme the impure, abraded nickel always showed some reaction, with the deposition of carbon and (in the cases where a direct test for carbon dioxide was made) the formation of carbon dioxide. The pure, abraded and impure electropolished samples represented intermediate cases in which there was occasional carbon deposition.

Typical plots of the experimental vapor-phase count rate against time are given in Fig. 2. In Experiment 10 the count rate fluctuated with time but a statistical analysis showed that the "best straight line" drawn had no significant slope; in contrast, in Experiment 11 there was clearly a statistically significant decrease in count rate, denoting the deposition of carbon upon the sample.

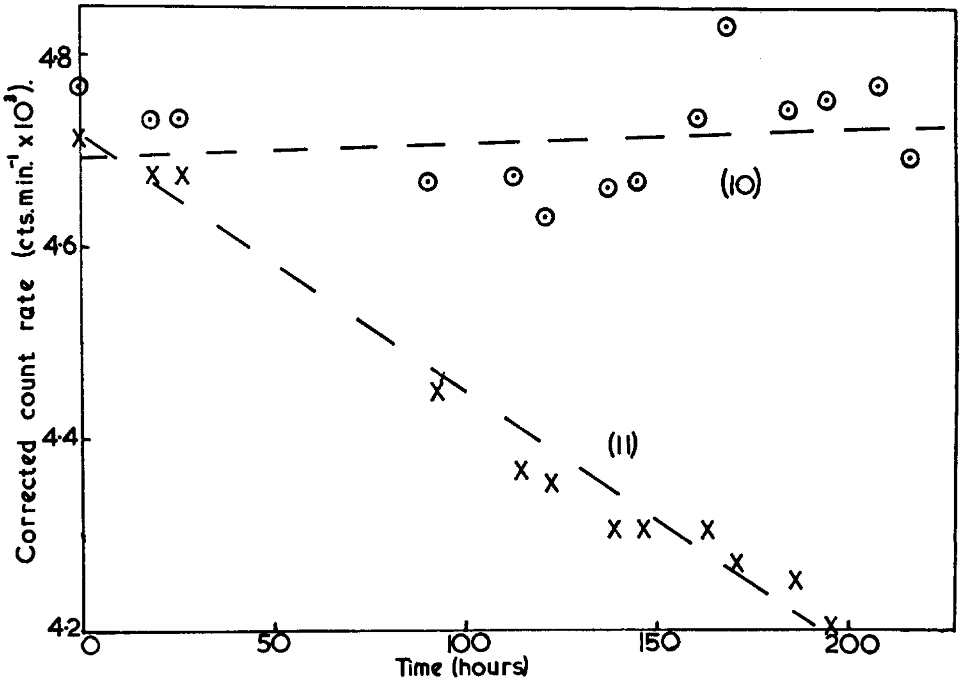

FIG. 2. Plot of corrected count rate against time for Experiments 10 and 11. For Experiment 10 the best straight line is given by the equation $Y = 0.10 \pm 0.15X + 4693 \pm 22$, i.e., no statistically significant change in count rate $Y$ with time $X$. For Experiment 11 the best straight line is given by $Y = -2.69 \pm 0.05X + 4715 \pm 11$, i.e., there was a statistically significant *decrease* in count rate with time.

Some typical curves of the weight of carbon deposited (calculated from the tracer results) as a function of time are given in Fig. 3.

## DISCUSSION

The two reactions which merit consideration as possible means for the deposition of carbon are

$$Ni + CO \rightarrow NiO + C \quad (1)$$

and

$$2CO \rightarrow C + CO_2 \quad (2)$$

As already indicated, however, reaction (1) can be ruled out for the temperatures examined: the equilibrium pressure of carbon monoxide is invariably higher than the experimental pressure, the disparity between the two values increasing markedly with increase in temperature.

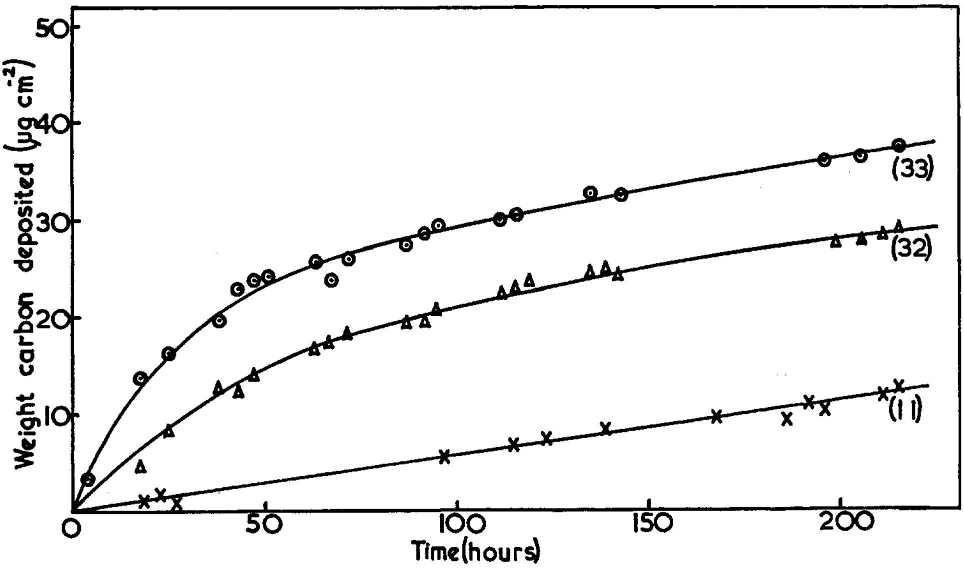

FIG. 3. Plot of weight of carbon deposited ($w$) against time for typical experiments ($w$ was calculated from the loss of counts from the gas phase).

The corresponding data (*1*) for reaction (2), given in Table 2, show that at all temperatures the proportion of carbon monoxide decomposed would, if equilibrium were reached, be sufficient to produce enough carbon to be experimentally detected. The absence of detectable amounts of carbon in the experiments listed in column 2 of Table 3 must be ascribed to the slowness of reaction (2) in the presence of electropolished metal; taken as a whole, the data of Table 3 strongly suggest that the disproportionation reaction is catalyzed by a nickel surface but only if it contains impurities or has undergone abrasion. The data of Table 3 are not sufficient, however, to assess the relative importance of these two factors.

The promoting effect of abrasion on the catalytic activity of the nickel can be plausibly attributed to the large number of dislocations produced in the surface layers by the abrasion process, for it is well known that, in general, the dislocations in a surface are the seat of enhanced chemical reactivity (*4*). The promoting action of impurities would then be explained in terms of a pinning of dislocations by the impurities. The process of electropolishing (*5*) removes the abraded layer—the Beilby layer; exposes the undisturbed regions of the bulk metal below; and thus produces a surface diminished catalytic activity.

An interesting alternative explanation suggests itself, however, when the results of Gwathmey and his collaborators (*6*) on the disproportionation of carbon monoxide on single crystals of nickel are considered; these workers found that the deposition of carbon occurred extensively on the (111) but not on the (100) and (110) faces of the crystal. Now if, as may well be the case (*5*), the Beilby layer is microcrystalline rather than truly amorphous, then one would expect all possible planes, including the catalytically active (111), to be exposed as a result of the random orientation of the crystallites. In the electropolished metal, on the other hand, the orientation imposed on the crystals by the rolling of the sheet metal (*7*), will ensure that only a very few preferred planes are exposed; and if it so happens that these do not include the (111) planes, then the absence of catalytic activity is explained. The effect of impurities can also be understood in terms of this model; for according to Pinsker (*5*) the stability of the microcrystalline layer, and in certain circumstances its ease of formation, are much enhanced by the inclusion of suitable impurity atoms.

If the microcrystalline model of the Beilby layer be accepted then the boundary regions between the microcrystallites are to be regarded as arrays of dislocations; and according to the first explanation it would then be these regions rather than the faces of the microcrystallites themselves that would be the seat of the catalytic activity. Which of the two explanations is correct cannot be decided on the basis of the evidence at present available.

Finally reference should be made to the fact that carbon—when deposited on the nickel by shadowing technique—fails to catalyze the disproportionation reaction; this does not necessarily rule out the possibility that the carbon deposited by the disproportionation reaction has catalytic properties [as found in the experiments of Strickland-Constable and Bromley (*8*)], because the state of subdivision of the carbon could differ significantly in the two cases. Indeed, the fact that the minimum deposit which can be detected in the present experiments corresponds to some eighty atomic layers of carbon would seem to support the idea of such catalytic activity: It would seem unlikely that diffusion of the carbon into the bulk of the nickel could occur with sufficient rapidity to leave bare substantial parts of the nickel surface.

## ACKNOWLEDGMENT

Thanks are offered to the United Kingdom Atomic Energy Authority (Harwell) for financial support.

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