

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON, NEW JERSEY]

## The Catalytic Oxidation of Carbon Monoxide on Nickel Oxide. I. Pure Nickel Oxide

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The reaction between carbon monoxide and oxygen was investigated on nickel oxide catalysts at different partial pressures of carbon monoxide and oxygen and temperatures up to 222°. After an initial stage characterized by high rates and rapidly diminishing activity, the catalyst shows a minimum constant value of activity. The kinetics of this latter stage changes above 180°. A reaction mechanism to explain the experimental data is derived. The concentration of excess oxygen in the solid phase is shown to be the controlling factor in determining the type of kinetics followed by the reaction.

Several metal oxides are known to contain oxygen in excess of the stoichiometric amount. The excess oxygen, which is often referred to as active oxygen, affects a large number of physico-chemical properties of these oxides.<sup>1</sup> The role played by active oxygen in oxidation catalysis has been recently studied by Krauss,<sup>2</sup> who was able to show that the formation of nitrous oxide from ammonia-oxygen mixtures is directly dependent on the oxygen content of the solid phase and independent of the type of oxide catalyst used. On the basis of these and previous results on a variety of oxidation processes it can be concluded that oxidation catalysis on these oxides does not proceed through alternate reduction-oxidation steps, involving the production of separate phases, but rather by means of the excess oxygen present on the surface, whose steady state concentration during catalysis is dependent on the partial pressure of the oxygen in the gas phase. It is therefore of interest in catalytic studies of oxidation reactions to investigate how the excess oxygen of the solid phase affects the over-all catalytic process. The present investigation represents an attempt to apply these considerations in deriving the kinetics of the oxidation of carbon monoxide on nickel oxide.

Previously, Bone and Andrews,<sup>3</sup> studying the same reaction on nickel oxide powder, found that the process could be described by a first order equation with respect to the total pressure. They concluded that the reaction occurs through the formation on the nickel oxide surface of a film of active oxygen, which in turn oxidizes adsorbed carbon monoxide. The same reaction was recently studied by Roginskii and Tselinskaya<sup>4</sup> on nickel oxide obtained from nickel carbonate. These authors were able to correlate the activity of the catalyst with the change in free energy occurring during the decomposition process of nickel carbonate.

## Experimental

**Materials.**—Nickel oxide samples were prepared in the following ways. C.P. nickel nitrate was decomposed for 3 hours at 300°, fired in air at 640° for an additional 3 hours, then slowly cooled to room temperature. The resulting gray-green oxide was found to liberate iodine from an acid

(1) M. Le Blanc and E. Möbius, *Z. physik. Chem.*, **A142**, 59 (1934); M. Le Blanc and H. Sachse, *Z. Elektrochem.*, **32**, 58, 205 (1926); *Verh. d. Sachs. Akad. Wissen. math. nat. klasse*, **63**, 1755 (1930); M. Le Blanc and G. Wehner, *Z. physik. Chem.*, **A168**, 165 (1934); C. Wagner and K. Hauffe, *ibid.*, **B44**, 181 (1938).

(2) W. Krauss and A. Neuhaus, *ibid.*, **B50**, 323 (1941); W. Krauss, *Z. Elektrochem.*, **53**, 320 (1948).

(3) W. A. Bone and G. W. Andrews, *Proc. Roy. Soc. (London)*, **110A**, 16 (1926).

(4) S. Z. Roginskii and T. S. Tselinskaya, *J. Phys. Chem., U.S.S.R.*, **22**, 1350 (1948).

solution of potassium iodide, to have a BET surface area of 2.2 m.<sup>2</sup>g.<sup>-1</sup> and to show an X-ray pattern of pure nickel oxide. According to Prasad and Tendulkar<sup>5</sup> this preparation of nickel oxide contains a large excess of oxygen. A second sample of nickel oxide was obtained under similar conditions except that decomposition and firing of the nickel nitrate was accomplished in an atmosphere of purified helium. Carbon monoxide, from a commercial tank, was purified by passing it through glass wool, soda lime and phosphorus pentoxide. This method of purification was found to give a gas sufficiently free of catalytic poisons, since, in preliminary tests, no difference in catalytic activity could be found using a gas purified with the above method or by low temperature distillation. Oxygen from a commercial tank was purified by passing it over calcium chloride, Pd-asbestos and phosphorus pentoxide.

**Apparatus.**—Rates of oxidation were observed in an all-glass, completely closed system, having a total volume of 302 cc. Weighed amounts of catalyst (0.05 ÷ 0.4 g., 20–30 mesh) were loaded in a small reactor, surrounded by an electrically heated coil. Reactor temperature was controlled ( $\pm 0.5^\circ$ ) by a gas thermoregulator. Premixed carbon monoxide and oxygen were forced to pass through the catalyst by means of an alternating mercury pump, driven by an electrical motor. Gold foils were placed in the apparatus to trap any mercury vapor which might pass in. The carbon dioxide formed could be removed by passing the gases through a column filled with Ascarite. Changes in pressure due to the reaction were recorded by means of a mercury manometer. The manometer readings, taken with the aid of a cathetometer, provided a means of following the extent of the reaction. In order to obtain data, independent of diffusion effects, several pumping speeds were tried, and a pumping speed of 10 cc. sec.<sup>-1</sup> was finally adopted. Generally runs were carried to ~30% conversion. Some runs however were carried to completion, and in cases where the initial ratio of CO:O<sub>2</sub> was different from the stoichiometric the final pressure agreed quite well with the pressure calculated from the initial pressure. The experimental error in the determination of the velocity constant,  $k$ , was  $\leq 9\%$ , and of the over-all activation energy,  $E$ ,  $\pm 1$  kcal./mole.

## Results

From the beginning of this study, it became clear that the catalyst was undergoing an irreversible change during the course of each run. However, after being used for a sufficient time, the activity of the catalyst reached a minimum value, which could be considered constant for all practical purposes. It was therefore concluded that, under the conditions of the experiment, two different stages for the catalytic process have to be recognized: (a) an initial stage characterized by high rates and rapidly diminishing activity, followed by stage (b) of constant activity. Both stages are kinetically distinguishable.

Data for stage (a) were found to obey a kinetic law of the type

$$dg/dt = ae^{-\alpha g} \quad (1)$$

where  $g$  is the amount of conversion and  $a$ ,  $\alpha$  constants. In Fig. 1 are presented some data on fresh

(5) M. Prasad and M. G. Tendulkar, *J. Chem. Soc.*, 1403 (1931).

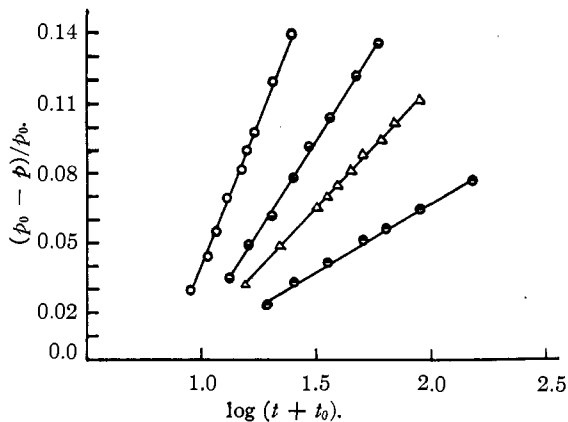


Fig. 1.—Initial rates of carbon monoxide oxidation on nickel oxide: (0.483 g.);  $p_{CO}$ , 186 mm.;  $p_{O_2}$ , 94 mm.: ●, 161°; △, 181°; ○, 200°; ○, 212°.

nickel oxide samples, plotted according to the integrated form of (1)

$$\log(t + t_0) = \alpha g - \log a \alpha$$

where  $t_0$  is a constant. Values for the parameters of equation (1), obtained at different temperatures, are collected in Table I.

TABLE I  
EFFECT OF TEMPERATURE ON THE INITIAL RATES OF CARBON MONOXIDE OXIDATION

| NiO, 0.483 g.; $p_{CO} = 186$ mm., $p_{O_2} = 94$ mm. |              |          |   |
|---|--------------|----------|---|
| $t$ , °C.   | $t_0$ , min. | $\alpha$ | $a$ , min. <sup>-1</sup> g. <sup>-1</sup> |
| 161   | 10           | 16.0     | 0.0063                                    |
| 181   | 10           | 9.75     | .0103                                     |
| 200   | 10           | 5.20     | .0200                                     |
| 212   | 9            | 3.80     | .0263                                     |
| 161   | 10           | 59.0     | .0017 <sup>a</sup>                        |

<sup>a</sup> Sample fired in a helium atmosphere.

The  $\alpha$ 's were found to decrease with increasing temperature, while the initial rates,  $a$ , obeyed the Arrhenius equation (Fig. 2), from which an over-all activation energy of 9.7 kcal./mole was calculated.

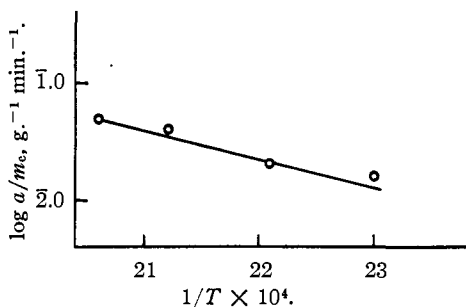


Fig. 2.—Initial rates of carbon monoxide oxidation on nickel oxide: Arrhenius plot;  $m_c$ , catalyst weight in grams.

Data for stage (b), obtained after prolonged treatment of the catalyst with the reacting mixture, were found to obey closely a first order equation with respect to the total pressure in the temperature region 100–180° (Fig. 3), whereas in the temperature range 180–240° the data could be better represented by an over-all kinetic order of  $\sim 1.25$ .

In Fig. 4 the values obtained in the high tempera-

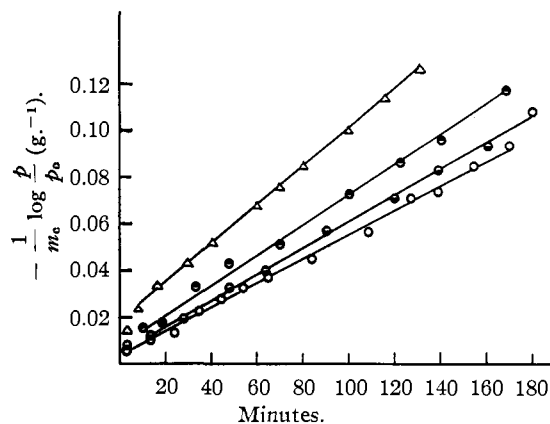


Fig. 3.—Carbon monoxide oxidation on nickel oxide:  $p_{CO}$ , 186 mm.;  $p_{O_2}$ , 94 mm.; low temperature range: ○, 106°; ●, 125°; ●, 147°; △, 174°.

ture region are plotted according to the integrated form of the equation

$$-dp/dt = kp^{1.25}$$

Velocity constant data in both temperature regions were found to fit the Arrhenius equation and to

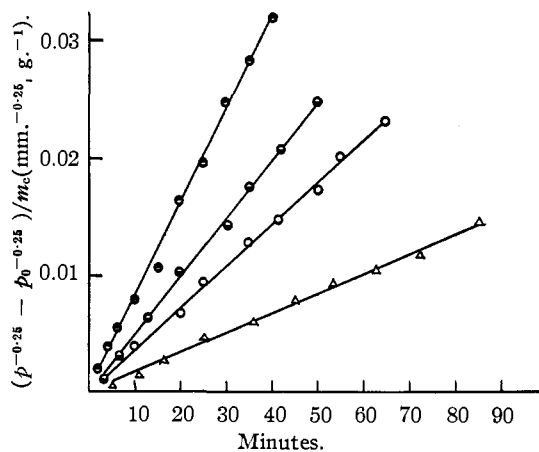


Fig. 4.—Carbon monoxide oxidation on nickel oxide  $p_{CO}$ , 186 mm.;  $p_{O_2}$ , 94 mm.; high temperature range: △, 181°; ○, 205°; ●, 222°; ●, 236°.

yield an activation energy of 2.2 kcal./mole for the low and 13.0 kcal./mole for the high temperature range (Figs. 5 and 6). Fresh catalyst samples were pretreated with carbon monoxide or oxygen for 1 hour at temperatures and partial pressures similar to those used in the kinetic experiments. After pretreatment the reaction chamber was evacuated and a fresh mixture of carbon monoxide and oxygen admitted. Pretreatment with carbon monoxide was found to eliminate stage (a) from the subsequent oxidation process, and the kinetic data thus obtained could be fitted with a first order equation. Rate values close to those obtained on catalysts after prolonged use were obtained. The data are collected in Table II.

No change in the initial rate of the oxidation reaction was detected by pretreatment of the catalyst with oxygen. The data obtained on the effect of different partial pressures of carbon monoxide

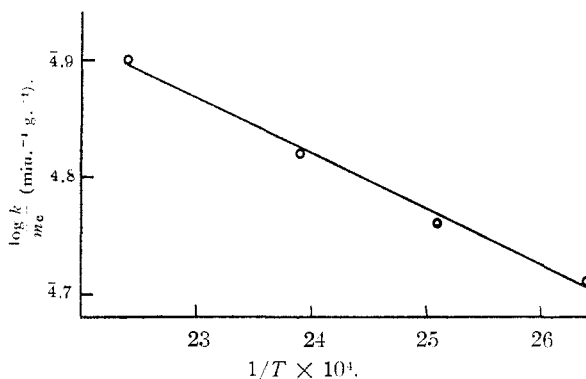


Fig. 5.—Carbon monoxide oxidation on nickel oxide: Arrhenius plot for the low temperature range.

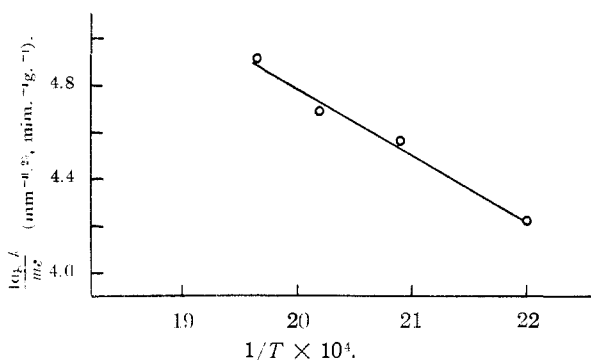


Fig. 6.—Carbon monoxide oxidation on nickel oxide: Arrhenius plot for the high temperature range.

TABLE II  
OXIDATION OF CARBON MONOXIDE BY OXYGEN ON NICKEL OXIDE. EFFECT OF CATALYST PRETREATMENT

| $t, ^\circ\text{C.}$ | $k \times 10^4, \text{ min.}^{-1} \text{ g.}^{-1}$ | Remarks   |
|----------------------|--|---|
| 106                  | 5.1  | Prolonged treatment of the catalyst               |
| 106                  | 5.5  | with reacting mixture                             |
| 106                  | 6.0  | Pretreatment of the catalyst with carbon monoxide |
| 106                  | 6.7  |   |
| 174                  | 7.9  | Prolonged treatment of the catalyst               |
| 174                  | 8.6  | with reacting mixture                             |

and oxygen on the rate of oxidation are summarized in Table III.

TABLE III  
EFFECT OF  $p_{\text{CO}}$  AND  $p_{\text{O}_2}$  ON THE RATE,  $v$ , OF CARBON MONOXIDE OXIDATION ON NiO

| $t, ^\circ\text{C.}$ | $v, \text{ mm. Hg min.}^{-1} \text{ g.}^{-1}$ | $p_{\text{CO}}, \text{ mm.}$ | $p_{\text{O}_2}, \text{ mm.}$ |
|----------------------|---|------------------------------|-------------------------------|
| 106                  | 0.140   | 186                          | 94                            |
| 106                  | .077  | 94                           | 45                            |
| 106                  | .195  | 186                          | 185                           |
| 106                  | .190  | 186                          | 186                           |
| 174                  | .220  | 186                          | 94                            |
| 174                  | .098  | 94                           | 45                            |
| 174                  | .310  | 186                          | 186                           |
| 174                  | .227  | 94                           | 186                           |
| 205                  | .565  | 186                          | 94                            |
| 205                  | .580  | 186                          | 186                           |
| 205                  | .298  | 94                           | 186                           |
| 222                  | 1.250   | 186                          | 94                            |
| 222                  | 0.600   | 94                           | 94                            |

From these data the values of  $k$  and  $\gamma$  in the equation  $-dp/dt = kp_{\text{O}_2}^\gamma p_{\text{CO}}^\gamma$  could be calculated. The following values were found:

| $t, ^\circ\text{C.}$ | $k$  | $\gamma$ |
|----------------------|------|----------|
| 106                  | 0.48 | 0.50     |
| 174                  | .52  | 0.54     |
| 205                  | ~ .2 | 1.10     |
| 222                  | .... | 1.05     |

The equations representing the experimental data are

$$-dp/dt = kp_{\text{O}_2}^{0.5} p_{\text{CO}}^{0.5} \quad (106-174^\circ) \quad (2)$$

and

$$-dp/dt = k' p_{\text{O}_2}^{0.2} p_{\text{CO}} \quad (205-222^\circ) \quad (3)$$

Carbon dioxide was found to have no effect on the rate in the high temperature range.

### Discussion

From the data presented it is clear that the oxidation process involves at least two kinetically different stages. Stage (a), represented by equation (1) can be suppressed by pretreating the catalyst with carbon monoxide but not with oxygen. This fact may be taken as an indication that the initial step consists in the removal by carbon monoxide of a large excess of surface oxygen, which is built into the catalyst during its preparation. It must be pointed out that the detrimental effect of carbon monoxide on the activity of the catalyst occurs in a temperature range where no lattice oxygen is readily removed. A similar effect, obtained by pretreatment of the catalyst with carbon monoxide, has already been described by Burns<sup>6</sup> for the oxidation of carbon monoxide on manganese dioxide.

A lower rate of oxidation is found on nickel oxide, which was fired in helium, as compared to samples fired in air. Since the former contains undoubtedly less excess oxygen than the latter, this fact is presented as supporting evidence for the previous explanation of the initial step of the oxidation process. The present results on the initial rates of oxidation agree with those of Roginskii and Tselinskaya,<sup>4</sup> who found that carbon monoxide oxidation on very active nickel oxide catalysts could be kinetically described by equation (1), while for less active catalysts the data could be fitted to a first order equation. Equation (1) has already been used to express the kinetics of a number of heterogeneous processes. Roginskii and co-workers<sup>7</sup> were able to describe the adsorption of carbon monoxide and its oxidation on manganese dioxide in terms of equation (1). Elovich and Zhabrova<sup>8</sup> found that ethylene hydrogenation on nickel together with the activated adsorption of ethylene and hydrogen on the same catalyst followed the same exponential law. More recently the derivation and interpretation of equation (1) have been discussed by Taylor and Thon,<sup>9</sup> who showed that a large number of

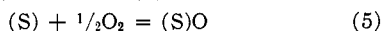
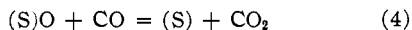
(6) N. Shurmovskaya and B. Burns, *J. Phys. Chem., U.S.S.R.*, **14**, 1183 (1940).

(7) S. Z. Roginskii and J. Zeldowitsch, *Acta Physicochim. U.S.S.R.*, **1**, 554 (1934); S. Yu. Elovich, S. Z. Roginskii and F. I. Kharakhurin, *ibid.*, **3**, 503 (1935).

(8) S. Yu. Elovich and G. M. Zhabrova, *J. Phys. Chem. U.S.S.R.*, **13**, 1761, 1775 (1939).

(9) H. A. Taylor and N. Thon, paper presented at the Meeting of the American Chemical Society, New York, September, 1951.

chemisorption processes can be described by equation (1). In the course of the initial step of the oxidation of carbon monoxide a strong interaction occurs between reactants and catalyst, some of the surface oxygen being irreversibly removed by carbon monoxide. If the over-all oxidation process is represented by the steps



where (S) is a bare surface site, the initial stage (a) is characterized by equation (4) which occurs faster than (5), due to the large initial excess of (S)O present. Supporting evidence for this fact can be obtained by considering the effect of the pretreatment, as previously discussed, of the catalyst with carbon monoxide. As the concentration of (S)O adjusts to that corresponding to the gas phase pressure of oxygen, the catalyst reaches a constant activity, characterized by the kinetics of stage (b). Then, if reaction (4) is slow compared with (5), the rate of (4) is given by

$$v_1 = k' p_{CO} \theta_{(S)O} \quad (6)$$

where  $\theta_{(S)O}$  is the fraction of surface occupied by adsorbed oxygen. From the experimental data it can be seen that both the oxygen and carbon monoxide affect the rate and therefore it is reasonable to assume that the surface is not wholly covered by any one of the reactants. Under these conditions it is possible to use the device introduced by Temkin and Pyzehv<sup>10</sup> in their treatment of ammonia decomposition, namely, the use of a virtual equilibrium pressure. Then

$$\theta_{(S)O} = \frac{p}{p + b}$$

where  $p$  is the partial pressure of oxygen fulfilling the gas phase equilibrium at a coverage  $\theta_{(S)O}$  of adsorbed oxygen, and  $b$  a constant. Equation (6) therefore becomes

$$v_1 = k_1 p_{CO} \frac{p}{p + b} \quad (7)$$

On the assumption that the surface is heterogeneous it is possible to apply to the present case the equation developed by Temkin and Kul'kova<sup>11</sup> for the water gas shift on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. In the case where the determining step of the reaction is similar to that considered here, these authors derive from equation (7) the following expression for the rate of the slow process

$$v_1 = k_1' p_{CO} p^\beta \quad (8)$$

where  $k_1' = (\pi/\sin \beta\pi) (G_1/f)$ ;  $G_1, f, \beta = \text{constants}$ ,  $0 < \beta < 1$ . But  $p = K_0(p_{O_2})^{1/2}/p_{O_2}$ , where  $K_0$  is the equilibrium constant of (5). Thus in the present case equation (8) becomes

$$v_1 = k_1' p_{CO} (p_{O_2})^{\beta/2} \quad (9)$$

Similarly, assuming that equation (5) is rate-determining one gets

$$v_2 = k_2' p_{O_2}^{1/2} (p_{CO}/p_{CO_2})^{\beta'} \quad (10)$$

It can be seen that equations (9) and (10) agree well with equations (2) and (3) derived from experimental data, with  $\beta = \beta' \cong 0.50$ . Therefore, it may be concluded that equation (4) represents the determining step for the high temperature interval, while equation (5) that for the low temperature range.

Additional proof for the validity of equation (9) to represent the experimental data is given by the fact that carbon dioxide was found to have no effect on the rate at high temperatures. Similar tests for equation (10) could not be carried out with the present experimental set up.

The above interpretation of the experimental data is consistent with the results of Wagner and Hauffe.<sup>12</sup> These authors on the basis of semi-conductivity data concluded that the controlling step for the carbon monoxide oxidation on nickel oxide at 700° is determined by the rate of carbon monoxide interaction with the nickel oxide surface. Supporting evidence for the validity of these deductions may be found in the effect of additions of foreign ions to nickel oxide on the activation energy of the oxidation reaction (see following paper). Less clear are the reasons for the reversal of the kinetics in passing from the low to the high temperature interval. Possibly this effect might be associated with different energy levels present in nickel oxide containing excess oxygen. Recent work of Wright and Andrews<sup>13</sup> shows the presence of two levels, 7 kcal./mole and 24 kcal./mole, which could be interpreted as a surface and bulk level, respectively, being therefore operative in a different temperature interval.

On the basis of the present results it can be concluded that during the oxidation of carbon monoxide on nickel oxide the concentration of excess oxygen in the solid phase is paramount in determining the type of kinetics followed by the oxidation reaction. Furthermore it is possible that the energy associated with that particular type of oxygen which is operative is responsible for changes in the over-all activation energy of the catalytic process.

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(10) M. I. Temkin and V. Pyzehv, *Acta Physicochim.*, U.R.S.S., **12**, 327 (1940).

(11) N. V. Kul'kova and M. I. Temkin, *J. Phys. Chem. U.S.S.R.*, **23**, 695 (1949).

(12) C. Wagner and K. Hauffe, *Z. Elektrochem.*, **44**, 172 (1938).

(13) R. W. Wright and J. P. Andrews, *Proc. Phys. Soc.*, 446 (1949).