Sorption of Gases on Evaporated Nickel Films. II. Adsorption and Decomposition of Carbon Monoxide at Low Pressures. Part 1

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Introduction

The adsorption of carbon monoxide by evaporated metallic films has already been investigated by several authors[1,2,3] it being known that carbon monoxide is chemisorbed without dissociation. However, some discrepancies are found among their views on the mechanism of adsorption. On the other hand, while a number of works[4,5,6,7] have been reported on the decomposition of this gas by reduced nickel catalysts, no attempt has been made on an evaporated nickel film. Since previous works have been carried out at higher pressures and on reduced nickel, elementary processes involved in the reaction have not yet been clarified.

The present work was undertaken to investigate the behavior of carbon monoxide molecules on a clean nickel surface at room temperature as well as at high temperatures above 100°C, which permitted one to discuss the special features of evaporated nickel film in catalytic activity. Part 1 of this series is confined to the adsorption at room temperature and the decomposition at high temperatures will be described in part 2.

Experimental

The apparatus and procedures used were essentially the same as in the previous papers[8,9], except that the films deposited on the wall of a glass bulb at 0°C were pre-sintered at 90°C for about ten minutes.

Carbon monoxide, made by dropping 85% formic acid on concentrated sulfuric acid in a flask which was heated at about 110°C and well evacuated before the generation of the gas, was purified by passing it through the following train; (1) 55% potassium hydroxide solution, (2) the same solution containing 4% pyrogallol, (3) concentrated sulfuric acid, (4) phosphoric acid anhydride, and (5) a liquid-oxygen trap.

Results and Considerations

1) **Adsorption Rate.**—Admitting the gas to the nickel film within the temperature range of −78 to 100°C, it is taken up in a similar way irrespective of the film temperature, and these uptakes shall be called *room-temperature-adsorption* and distinguished from *high-temperature-decomposition* which will be mentioned in part 2 of this series.

As shown in Fig. 1, the adsorption of carbon monoxide comprises two stages, i.e., an initial rapid stage and a later slow one. At the initial stage, the pressure change was too rapid to be followed by the Pirani gauge in the first one minute after admission of gas, but the rate appeared to be substantially constant irrespective of the adsorbed amount. At the later stage, on the other hand, the rate becomes slow with the amount of successive adsorption.

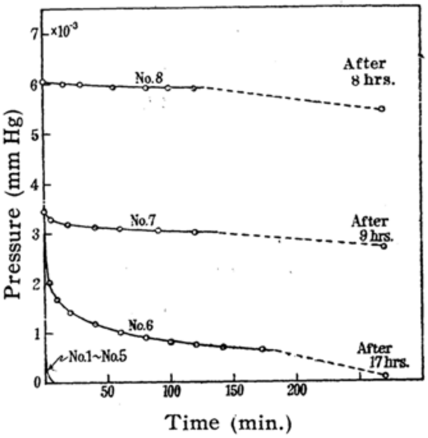

Fig. 1. Rate curves of adsorption at 0°C.

Setting the apparent rate of pressure decrease in the later stage $-\frac{dp}{dt}$ equal to the rate of adsorption r_a, we can plot $\log r_a$ against the adsorbed amount v for curve 6 in Fig. 1, in which the rate begins to decrease with v appreciably. Then a linear

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[1] (a) O. Beeck, A. E. Smith and A. Wheeler, *Proc. Roy. Soc.* (*London*), *A*, 177, 62 (1940); (b) O. Beeck, "Advances in Catalysis" Vol II, Academic Press Inc. New York, 1950, p. 151.

[2] E. K. Rideal and B. M. W. Trapnell, *Proc. Roy. Soc.* (*London*), *A*, 205, 409 (1951).

[3] A. S. Porter and F. C. Tompkins, ibid., A, 217, 529, 544 (1953).

[4] H. A. Bahr and Th. Bahr. *Ber.*, 61, 2177 (1928).

[5] S. Horiba and T. Ri, *Rev. Phys. Chem. Japan*, 4, 73 (1930); T. Ri, ibid., 5, 41 (1931).

[6] H. Tsuchiya, *Bull. Inst. Phys and Chem. Research*, 10, 951 (1931).

[7] T. Kwan and T. Izu, *Catalyst*, no. 6, 43 (1949).

[8] Z. Oda, *Oyobutsuri* (*J. Appl. Phys. Japan*), 22, 142 (1953).

[9] Z. Oda, This Bulletin, 27, 467 (1954).

relation is obtained as shown in Fig. 2, from which the rate is represented as a function of v by

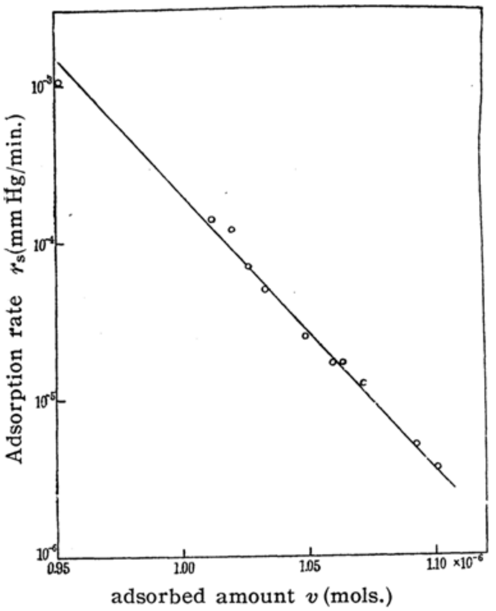

Fig. 2. The rate of adsorption as a function of adsorbed amount.

$$\ln r_a = \ln a - \alpha v, \tag{1}$$

The Elovich equation[10] is thus derived.

$$r_a = a\, e^{-\alpha v}. \tag{2}$$

As $r_a = \dfrac{dv}{dt}$, integration of Eq. (2) gives

$$v = 1/\alpha\{\ln(t+k) - \ln t_0\}, \tag{3}$$

where $k = \exp(av_0)/a\alpha$, $t_0 = 1/a\alpha$ and v_0 is the amount already taken up before $t=0$. Using p instead of v and plotting p against $\log(t+k)$ for the result shown in Fig. 2, the validity of Eq. (3) is tested in Fig. 3, where the value of k is selected to smooth the plot. The slope of this line gives $2.3/\alpha$. Values of α thus calculated from Figs. 2 and 3 are 4.09×10^7 mol.$^{-1}$ and 4.42×10^7 mol.$^{-1}$, respectively, showing a good agreement with each other. Furthermore, if one assumes $v_0=0$ at $t=0$, it is given from Eq. (3) that $t_0=k=1.3$ min. and so the initial rate a is calculated to be about 1.8×10^{-8} mol./min. from the relation $t_0=1/a\alpha$. This value shows a good coincidence with the observed one 5.6×10^{-8} mol./min. obtained from Fig. 2. This fact indicates the assumption $v_0=0$ at $t_0=0$ to be probable, i. e., the rapid adsorption preceding the slow one is not included in Eq. (2).

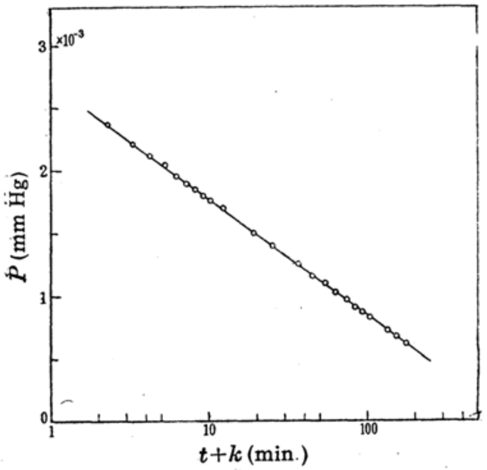

Fig. 3. $p-\log(t+k)$ plot $k=1.3$ min.

When the adsorption increases still more, the rate is expressed by

$$r_a = \beta(p - p_e), \tag{4}$$

where β is a rate constant and p_e is an equilibrium pressure.

2) Adsorption Equilibrium. — The initial stage where the adsorption rate was very rapid gave equilibrium pressures of 10^{-6} to 10^{-5} mmHg, but at the later stage, the equilibrium was not readily attained. After measuring a rough adsorption isotherm up to a pressure of about 5×10^{-2} mmHg, the system was evacuated to high vacuum. On admitting a dose of gas again, the rapid uptake was not observed but the slow one alone took place. Therefore, it is reasonable to consider that the initial stage is an irreversible adsorption and the later stage includes a reversible one; hence the calculation of isothermal heat of adsorption is not possible at the initial stage.

Now the Langmuir adsorption isotherm may be written in the form

$$p/v = 1/v_m b + p/v_m, \tag{5}$$

where b is an adsorption coefficient and v_m the amount adsorbed at saturation. Thus, as shown in Fig. 4a, plotting p/v against p for an isotherm, two straight lines intersecting at about 1×10^{-4} mm Hg are obtained. Fig. 4b shows the data below this pressure on enlarged scales. From the slopes and intercepts at p/v -axes in Figs. 4a and 4b, v_m and b can be calculated for both pressure ranges. For lower pressure range $v_{m1} = 1.15\times10^{-6}$ mol. and $b_1 = 4.97\times10^5$ mm Hg^{-1}; for higher range $v_{m2} = 1.29\times10^{-6}$ mol. and $b_2 = 3.87\times10^3$ mm Hg^{-1}. These results suggest that there exist two sites with different adsorption coefficients on the surface of the nickel film. In such a case, the adsorption isotherm is generally expressed by[11]

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[10] S. Yu. Elovich and G. M. Zhabrova, *Zhur. fiz Khim.*, 13, 1761, 1775 (1939).

[11] S. Brunauer, "Adsorption of Gases and Vapors, Physical Adsorption", Princeton Univ. Press, Princeton, 1945, p. 74.

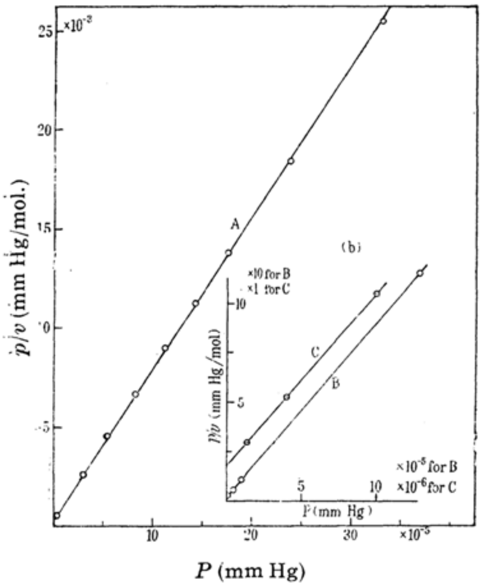

Fig. 4. Adsorption isotherms at 0°C plotted according to the Langmuir equation
(a) high-pressure range.
(b) low pressure range.

$$v=\frac{v_1b_1p}{1+b_1p}+\frac{v_2b_2p}{1+b_2p} \tag{6}$$

In the present case, we can set $v_1=v_{m1}$, $v_2=v_{m2}-v_{m1}$ and $b_1 \gg b_2$. If p is small, the second term of the right-hand becomes negligible compared with the first term. So that

$$v \simeq \frac{v_1b_1p}{1+b_1p}, \tag{7}$$

which indicates that the adsorption takes place exclusively on the sites with larger adsorption coefficient. On the other hand, if p becomes large, it follows $b_1p \gg 1$, so that

$$v \simeq v_1+\frac{v_2b_2p}{1+b_2p} \tag{8}$$

which shows that the subsequent adsorption occurs on the remaining sites with smaller adsorption coefficient.

The amounts of rapid adsorption and the total one measured with several films at 0°C are summarized in Table I. The ratio of the rapid adsorption to the total one is about 80% and the average value of the latter is 3.92×10^{-6} mol./10 mg. Ni.

Discussions

Porter and Tompkins[3] have found the Elovich equation to be applicable to the rate of uptake of hydrogen and of carbon monoxide by evaporated iron films between 78 and 140°K. In order to interpret these results they have considered the total process involving the initial rapid process to be a united process, by assuming that the iron film has a heterogeneous surface with sites of different adsorption potential and activation energy required for adsorbed molecules to migrate, so that the sticking of gas molecules must proceed from sites of lower activation energy to sites of higher. However, as mentioned above, in the adsorption of carbon monoxide as well as in the case of oxygen[9], the rate of uptake in the initial stage is very rapid and substantially constant, independent of the adsorbed amount; in the case of the former this rapid adsorption amounts to about 80% of the total adsorption, after which the rate falls with the increase in adsorption. Furthermore, Eq. (2) has been proved to be applicable to the beginning of the later stage only.

From these facts, another interpretation for Eq. (2) than that of the above authors is desirable. Davis[12] has shown that in the chemisorption of nitrogen on tungsten the activation energy E increases with surface coverage θ. Recently Zwietering and Roukens[13] have also observed the same relation in the chemisorption of nitrogen on iron. If such a relation is assumed to exist in the present system, we may write

$$E(\theta)=E_0+\gamma\theta, \tag{9}$$

TABLE I

INITIAL ADSORPTION AND TOTAL ADSORPTION OF CO AT 0°C

Equil. pressure	Evaporated amount	Rapid adsorption	Total adsorption		Rapid adsorption / Total adsorption
			(obs.)	(per 10mg. Ni)	
$\times10^{-2}$ mm Hg	mg.	$\times10^{-6}$ mol.	$\times10^{-6}$ mol.	$\times10^{-6}$ mol.	%
3.5	3.3	1.12	1.38	4.18	81.3
3.5	3.3	1.10	1.34	4.06	82.1
4.3	3.2	0.99	1.21	3.78	81.8
8.5	3.4	1.00	1.25	3.68	79.9
			(average)	3.92	81.3

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[12] R. Davis, *J. Am. Chem. Soc.*, **68**, 1395 (1946).

[13] P. Zwietering and J. J. Roukens, *Trans. Farad. Soc.*, **50**, 178 (1954).

where E_0 is the activation energy at the initial stage.

It is well known that carbon monoxide is adsorbed on evaporated metallic films as molecules[1,2,3]. Hence, the rate is generally given by the following equation

$$r_a = kp(1-\theta)e^{-E(\theta)/RT}. \tag{10}$$

Substituting for $E(\theta)$ from Eq. (9),

$$r_a = kp\, e^{-E_0/RT}(1-\theta)\, e^{-(\gamma/RT)\theta}. \tag{11}$$

In the isothermal adsorption, if p is constant or its change is small, it is possible to set $kp\, e^{-E_0/RT} = a_0$ and $\gamma/RT = \alpha_0$. Then Eq. (11) reduces to

$$r_a = a_0(1-\theta)\, e^{-\alpha_0\theta}. \tag{12}$$

When α_0 is so large that the change of $(1-\theta)$ can be negligible compared with that of $e^{-\alpha_0\theta}$, Eq. (12) may be approximately represented by the expression

$$r_a = a\, e^{-\alpha_0\theta}, \tag{13}$$

which is formally identical with Eq. (2).

In terms convenient for application to the data shown in Fig. 2, Eq. (9) can be written in the form

$$E(v) = E_0 + \gamma' v.$$

Since $\alpha = 4\times10^7$ mol.$^{-1}$ and $RT = 2\times273 = 546$ cal./mol., we obtain $\gamma' = \alpha RT = 2.2\times10^{10}$ cal./mol.^{2} In addition, since the amount adsorbed in this run is $v = 1.5\times10^{-7}$ mol., the activation energy for the final part of this run is given by

$$E = E_0 + 3.3 \text{ kcal./mol.},$$

i.e., the activation energy increases by 3.3 kcal./mol. during this adsorption.

On the other hand, it is found from the adsorption isotherms that the surface of nickel film comprises two areas with sites differing in their adsorption coefficients and these areas correspond to the rapid and slow adsorption, respectively. According to Beeck[1], the heat of adsorption of carbon monoxide on nickel film is 35 kcal./mol. and constant over 85% of the surface coverage, after which it falls abruptly to a very low value. Hence, it is reasonable to consider the heat of adsorption at the initial stage equal to 35 kcal./mol. and that at the later stage corresponding to a very low value.

For the explanation of the over-all process of adsorption in connection with the surface character of the films, we assume the surface to comprise two areas A and B. Area A has sites of high heat of adsorption Q_A and the adsorption on these requires a small activation energy E_A; area B has sites of low heat of adsorption Q_B and for these the corresponding energy E_B is large: between these quantities we have the relation $Q_A > Q_B$ and $E_A < E_B$. On admitting an amount of gas to a fresh film, gas molecules colliding at random against the surface will be adsorbed exclusively by A at the initial stage. After A has been completely covered with gas molecules, the adsorption on B will begin. However, E_B is so large compared with E_A, that this process can be expected to be slow. These deductions would lead to a view that the initial and later stages correspond to A and B, respectively, i.e., the ratio of A to the total area is about 80% and the remainder corresponds to area B. However, it may be assumed that there exist some adsorption sites with various intermediate values of Q and E between those for A and B. Hence Eq. (2) is interpreted to represent the adsorption rate on these sites. On the other hand, when the remaining area becomes B alone, it is possible to set $\gamma = 0$, $E_0 = E_B$ and $\theta = \theta_B$ the coverage fraction of B. Then Eq. (11) becomes

$$r_a = kp(1-\theta_B)\, e^{-E_B/RT}. \tag{14}$$

At constant temperature and if p is nearly constant or its change is small, Eq. (14) reduces to

$$r_a = \beta_0(1-\theta_B), \tag{15}$$

with $\beta_0 = kp\, e^{-E_B/RT}$. This equation is equivalent to Eq. (4). Thus the adsorption of carbon monoxide on nickel films may be satisfactorily interpreted in terms of the non-uniformity of the surface throughout its over-all process.

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