Sorption of Gases on Evaporated Nickel Films. III. Adsorption and Decomposition of Carbon Monoxide at Low Pressures. Part 2

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Introduction

As mentioned in part 1[1] of this series, carbon monoxide was merely chemisorbed by nickel films under 100°C. However, with the rise of temperature above 130°C., carbon monoxide was found to be decomposed to carbon dioxide and atomic carbon which reacted with nickel atoms to give nickel carbide. In this report the kinetics of decomposition is discussed on the basis of the non-uniformity of the surface.

Experimental

In order to determine the quantity of carbon dioxide produced by the decomposition of carbon monoxide, the apparatus used was partially modified as shown in Fig. 1. The reaction bulb was connected to the gas handling system through two cold traps T_1, T_2 and a "greaseless cock" C. During the reaction these traps were cooled with liquid-oxygen. The carbon dioxide produced was condensed onto the inside wall of T_2. Closing the "greaseless cock" C by means of an electro-magnet and removing the liquid-oxygen from T_2, the increase in pressure in the volume of BPT_2 could be measured by the Pirani gauge P. As will be mentioned below, since carbon dioxide was not adsorbed by nickel films covered with the carbon monoxide layer of rapid adsorption, the amount of carbon dioxide liberated was evaluated[2] from the rise in pressure.

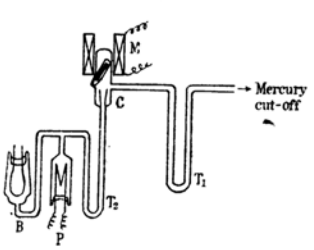

Fig. 1. The reaction apparatus.
B. Evaporation bulb; T_1, T_2. Cold traps
P. Pirani gange; C. Greaseless cock;
M. Electro-magnet.

In order to study the changes of the film structure after reaction, a small piece of cover glass for the microscope slide was previously set in the bulb, on which the nickel film was also deposited. When the reaction was finished, this piece was taken out as a sample for electron diffraction study. The films used in this experiment were pre-sintered for about thirty minutes at the same temperatures as those of the reaction.

Results and Considerations

1) Production of Carbon Dioxide.— Changing the reaction temperature in turn from 100 to 250°C for each gas admission, the pressure change was followed. Fig. 2 shows the rate curves in log P vs t plots. We see that at the later stage the plots at 100°C are slightly convex, linear at 130°C and slightly concave towards t-axis at 150[3] and 200°C, whereas at 250°C the plot yields a straight line except below the pressure of 3×10^{-4} mmHg. With the "greaseless cock" closed and liquid-oxygen removed from T_2, a remarkable rise in pressure was observed above 130°C. Even if the trap was cooled again by dry ice, pressure change was hardly observed. Furthermore, mass-spectrometric analysis[4] proved this condensable gas to be carbon dioxide. Hence, it became evident

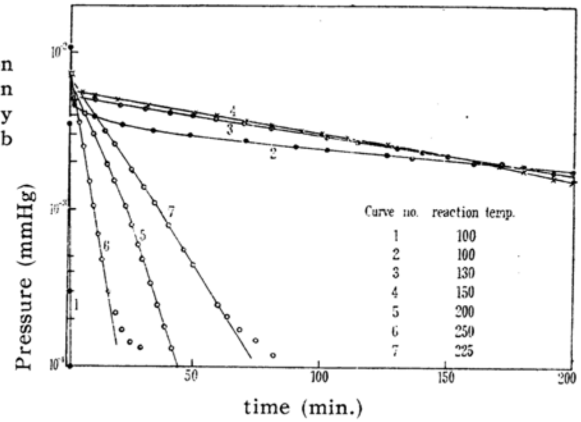

Fig. 2. Reaction rate curves at various temperatures.

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[1] Z. Oda, This Bulletin, 28, 281 (1955).

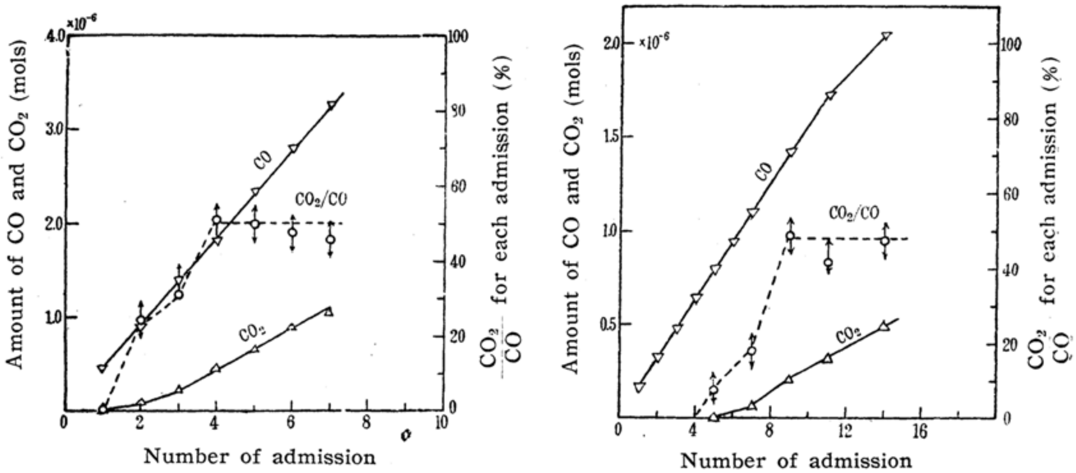
[2] Allowance were made for the difference in temperature of each part and the leak of the "greaseless cock". The accuracy was about ±5%.

[3] In this case, since the amount of carbon produced before this run was very small, it was considered that the diffusion of carbon took place readily, and the behavior was similar to that at 200°C.

[4] A small gas reservoir with a "magnetic-slug-break-off" was previously inserted ahead of trap T_2. After reaction the gases condensed in trap T_2 were collected in this reservoir by transferring liquid-oxygen from T_2 to it, and then it was sealed off and analysed.

that carbon monoxide was decomposed on nickel film above 130°C.

On admitting the gas to a fresh film at a constant temperature, the rate of pressure change and the amount of carbon dioxide produced in each run was measured. These results obtained at 200 and 150°C are given in Figs. 3a, 3b, 4a and 4b. As shown in Figs. 3a and 3b, at the initial stage, carbon dioxide was not observed immediately after the reaction had ceased. This was also the case, even if the film was kept for several hours at that temperature. With repetitions of reaction, the ratio of the amount of carbon dioxide to that of carbon monoxide consumed in one run (denoted by CO_2/CO) increases to 40~50%, which suggests that the reaction $2CO = CO_2 + C$ occurs quantitatively on nickel films. Comparing these behaviors with the rate curves at 200°C shown in Fig. 4a, it is seen that run 1 represents the curve of adsorption, runs 2 and 3 the rate curves comprising the adsorption and decomposition, and the runs after 4 are regarded as being of decomposition itself. In a example at 150°C shown in Fig. 4b, a similar state of affairs occurs, i.e., the runs after 9 are the rate curves of decomposition. However, the log P vs t plots show linear relation at pressures above 10^{-4} mm Hg in order. At 250°C, on the other hand, while the ratio CO_2/CO changes in a manner similar to that at 200°C, the rate curves are linear between 1×10^{-2} and 3×10^{-4} mm Hg and slightly concave towards t-axis in higher pressure range than 1×10^{-2} mm Hg.



(a) 200°C. (b) 150°C.

Fig. 3. The ratio of the amount of CO_2 produced to that of CO consumed.

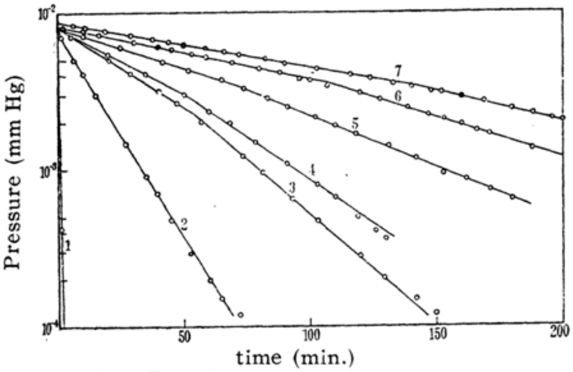


Fig. 4a. Reaction rate curves at constant temperature. (T=200°C)

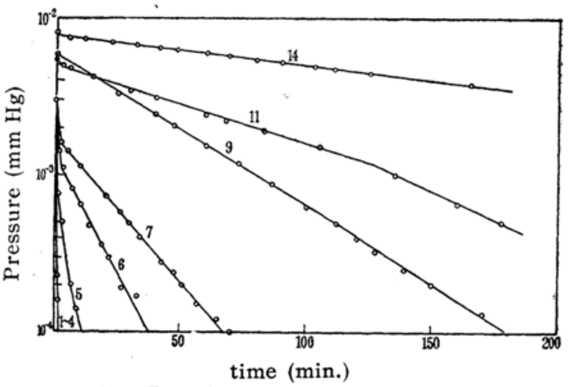


Fig. 4b. Reaction rate curves at constant temperature. (T=150°C)

2) The Initial Stage.—Prior to considerations of the rate of decomposition, we shall first compare the initial rapid adsorption with the total adsorption at high temperatures. The total adsorption[5] 3.92×10^{-6} mol./10 mg

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[5] This is defined as the amount taken up at 0°C and $P \doteqdot 5\times10^{-2}$ mm Hg as mentioned in part 1.

Ni shown in part 1 of this series is the average value for several films pre-sintered at 90°C for ten minutes. In the present case, however, since the films have been pre-sintered at higher temperatures, their available areas should be decreased. Fig. 5 shows the variation of the total adsorption with pre-sintering temperature when the films have suffered pre-sintering for thirty minutes. These results are listed in Table 1, from which the initial adsorption is found to occupy 70∼80% of the available area and to be almost independent of the reaction temperature.

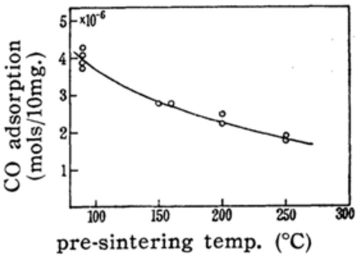

Fig. 5. Variation of total adsorption with pre-sintering temperature.

TABLE I

INITIAL RAPID ADSORPTION OF CO AT HIGH TEMPERATURES BEFORE DFCOMPOSITION

React. temp.	Evaporated amount	Rapid adsorption (obs.) (per 10 mg. Ni)		Total adsorption* (per 10 mg. Ni)	(Rapid adsorption) / (Total adsorption)
°C	mg.	10^{-6} mol.	10^{-6} mol.	10^{-6} mol.	%
150	3.3	0.65	1.97		
	3.5	0.71	2.03		
	2.8	0.78	2.78		
(average)			2.33	2.9	80.3
200	3.2	0.52	1.62		
	2.3	0.39	1.69		
	3.0	0.49	1.65		
	3.6	0.56	1.56		
	2.8	0.46	1.64		
	3.6	0.57	1.58		
(average)			1.62	2.25	73.2
250	3.0	0.41	1.37		
	3.5	0.48	1.37		
(average)			1.37	1.8	76.1

*) Average values obtained from Fig. 5.

However, it was not evident whether carbon monoxide was adsorbed with or without decomposition at the initial stage. While it was noted by previous authors that at high temperatures carbon dioxide was hardly adsorbed[6,7] on a nickel surface or slightly adsorbed[8] with dissociation even at 30°C, their experimental conditions differed substantially from the present author's. Hence, an attempt was made to make sure whether carbon dioxide was adsorbed on nickel film or not. After cooling only the trap T_2 with dry ice instead of liquid-oxygen, a dose of carbon dioxide was admitted to the film at 150 and/or 250°C. When the surface was clean or partially covered with carbon monoxide, rapid adsorption was observed. However, no adsorption was found after the rapid adsorption of carbon monoxide had been completed. This fact suggests that in the initial stage, if any carbon dioxide is formed, it is also adsorbed on nickel film and does not condense in the trap cooled with liquid-oxygen. Hence, it is impossible to decide the adsorbed state of carbon monoxide on nickel film. However, it may be possible to conclude that carbon monoxide and or its degradation products are strongly bounded by film surface and not readily desorbed until the surface is covered to 70∼80% of its available area.

3) The Later Stage.—As mentioned above, the amount of carbon monoxide consumed in one run is wholly converted to carbon dioxide after the reaction has been repeated many times, and thus considerations will be made in such a case.

Now we start on the assumption that the decomposition of carbon monoxide on the

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[6] N. Nikitin, *Z. anorg. Chem.*, **154**, 130 (1926).

[7] S. Horiba and T. Ri, *Rev. Phys. Chem. Japan*, **4**, 41 (1930).

[8] J. A. Dillon and H. E. Farnsworth, *Phys. Rev.*, **94**, 753 (1954) ; *J. Chem. Phys.*, **22**, 1601 (1954).

surface of nickel film proceeds through the following elementary processes:

1) $CO\ (g) \rightleftarrows CO\ (ads)$,
2) $CO\ (ads) \rightarrow (C-O)^{\ddagger}$,
3) $CO\ (g) + (C-O)^{\ddagger} \rightarrow CO_2(g) + C\ (atom)$,
4) $C\ (atom) + Ni \rightarrow Ni_3C$,

where $(C-O)^{\ddagger}$ represents the activated state of a carbon monoxide molecule. Assuming the reaction 2) to be the rate-determining step, the reaction will be of the first order with respect to the adsorbed amount of carbon monoxide v. Hence the rate is given by

$$-dP/dt=k_1 v \qquad (1)$$

Let θ_{co} and θ_c denote the fraction of the adsorption sites covered by carbon monoxide and carbon[9], respectively, then $(1-\theta_{co}-\theta_c)$ gives the fraction still bare at a given time. The corresponding adsorption isotherm is given by

$$\frac{\theta_{co}}{1-\theta_{co}-\theta_c}=bP. \qquad (2)$$

Hence

$$\theta_{co}=\frac{(1-\theta_c)\,bP}{1+bP},$$

or, using v instead of θ_{co},

$$v=\frac{(1-\theta_c)v_m bP}{1+bP}, \qquad (3)$$

where v_m is the amount of carbon monoxide corresponding to the total adsorption sites. Upon substituting this value for v in Eq. (1), we obtain

$$-dP/dt=k_1(1-\theta_c)v_m bP/1+bP. \qquad (4)$$

Since the rate curves obtained is apparently of different form depending on temperature, we shall consider each case.

i) 200°C.

In this case, since carbon formed on the surface is considered to diffuse rapidly to interior, the rates of its production and disappearance from the surface balance with each other at a given θ_c. Hence, θ_c may be taken as nearly constant during the reaction period of one admission, and thus Eq. (4) can be reduced to

$$-dP/dt=k_2P/1+bP, \qquad (5)$$

where

$$k_2=k_1(1-\theta_c)bv_m. \qquad (6)$$

Intergation of Eq. (5) gives

$$\ln P+bP=C-k_2t, \qquad (7)$$

or

$$\log P+(b/2{,}3)P=C'-(k_2/2{,}3)t. \qquad (8)$$

This means that if b is sufficiently large the $\log P$ vs t plot should be concave towards t-axis (cf. Fig, 4a). In order to apply Eq. (8) to the experimental data, it is necessary to obtain the value of b. By assuming that as the reaction time increases the term $(b/2.3)P$ becomes negligible compared with the absolute value of $\log P$ in the pressure range studied, Eq. (8) will be reduced to

$$\log P=C'-(k_2/2{,}3)t. \qquad (9)$$

Therefore, in Fig. 4a, by extrapolating the curve at large t towards a smaller one and setting the extrapolated value at any time t to be G, a plot of $G-\log P$ vs P is obtained as shown in Fig. 6. The slope of this line gives $b/2.3$. Thus, plotting $\log P+(b/2.3)P$ against t for the data shown in Fig. 4a, good straight lines are obtained as shown in Fig. 7. Although the value of b is nearly constant, independent of the repetition of reaction, the slope of lines, i.e., k_2 decreases with reaction. According to the relation (6) this is attributed to the increase of θ_c, i.e., a blocking effect by the carbon produced.

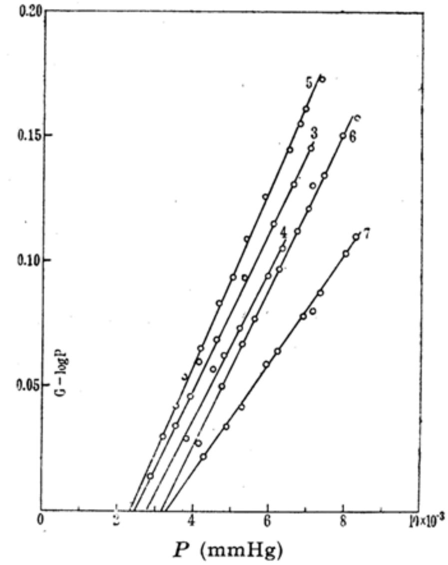

Fig. 6. G − log P vs P plots.

ii) 150°C.

From the definition of b it is anticipated that the bends in the $\log P$ vs t plots at this temperature must appear in a lower pressure range than at 200°C. This is evident by comparing Fig. 4b with Fig. 4a.

On the other hand, since the diffusion of carbon seems to be slower than at 200°C k_2 should not be constant but should decrease with time even in one run. Therefore, it is probable that the tendency to become concave towards t-axis due to the neglet of $(b/2.3)P$ term is just compensated by the decrease of k_2, and thus the plots yield straight lines

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[9] This includes atomic carbon and nickel carbide (Ni_3C) remaining on the surface.

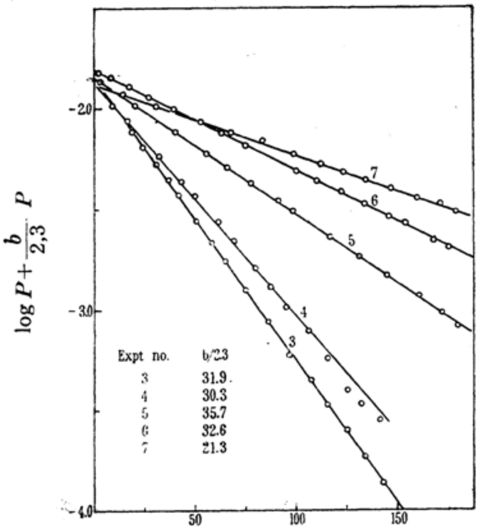


Fig. 7. $\log P+\dfrac{b}{2,3}P$ vs t plots.

above 1×10^{-3} mm Hg pressure. Consequently the plots of $G-\log P$ vs P are not represented by straight lines giving the value of $b/2.3$. Although it is impossible to analyse the reaction rate more precisely, Eq. (4) seems to hold for this case also.

ii) 250°C.

In this case, b is so small that the bend due to $(b/2.3)P$ term is not observed below 1×10^{-2} mm Hg. For example, a value of b derived from a rate curve above this pressure is 15 $(\text{mm Hg})^{-1}$, from which it follows $bP=0.075$ at $P=5\times10^{-3}$ mm Hg. Thus neglecting bP compared to 1 in Eq. (5), we find

$$-dP/dt=k_2P\,, \tag{10}$$

i.e., the reaction becomes of the first order type in agreement with experimental results.

4) **Heat of Adsorption and Activation Energy of Decomposition.**—Let Q and E_2 be the heat of adsorption and the apparent activation energy of the reaction, respectively, the temperature dependencies of b and k_2 are given by

$$b=b_0e^{Q/RT} \quad \text{and} \quad k_2=k_{20}e^{-E_2/RT}\,. \tag{11}$$

Therefore, at two temperatures, for example 200 and 225°C, the rates of decomposition were measured on the same film and b was evaluated by the procedure noted above. From plots of $\log b$ vs $1/T$ and $\log k_2$ vs $1/T$ for two films, the average values of Q and E_2 were found to be about 20.5 ± 1.4 and 14.6 ± 0.7 kcal/mol., respectively.

In addition, the temperature dependency of k_1 is given by

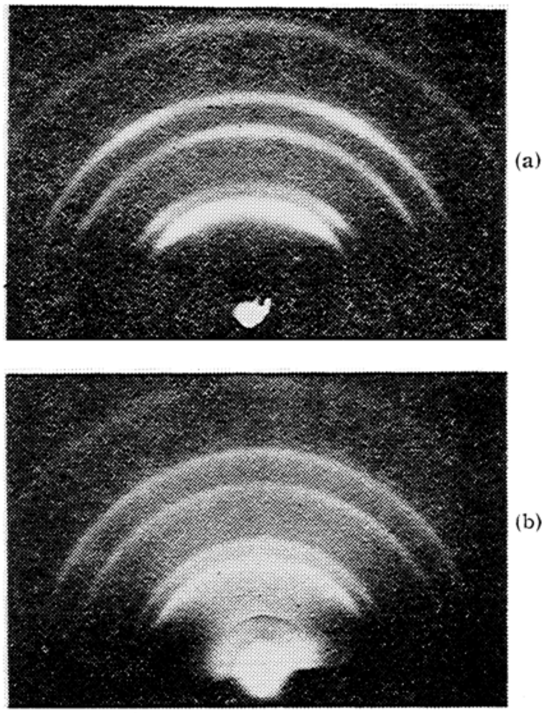
$$k_1=k_{10}e^{-E_1/RT}\,. \tag{12}$$

Hence, from Eqs. (6), (11) and (12) we can obtain a relation

$$E_2=E_1-Q\,. \tag{13}$$

With the values of Q and E_2 obtained above, it follows $E_1=35.1\pm2.1$ kcal/mol., which may be regarded as the potential energy difference between the activated state and the adsorbed state of the reactant. It is interesting to note that this energy is nearly equal to the heat of adsorption[10] at the initial stage where the decomposition cannot be detected.

5) **Electron Diffraction Study.**—After the reaction had been carried out under various conditions, electron diffraction photographs were taken with six films. If the ratio of the number of reactant molecules consumed to that of nickel atoms deposited was less than about 20%, the nickel pattern alone was observed, but if this ratio reached to about 40%, nickel carbide (Ni_3C) pattern[11] was also revealed in addition to that of nickel. The electron diffraction photographs before and after reaction are shown in Fig. 8.



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[10] See part 1.

[11] This was analysed by X-ray diffraction data given by A. Cimino and G. Parravano, *J. Phys. Chem.*, **56**, 706 (1952).

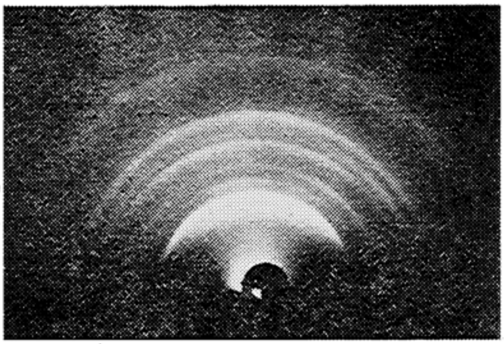

Fig. 8. Electron diffraction patterns of evaporated nickel films before and after reaction. (a) Pre-sintered at 100°C. for 1 hr. (b) After reaction at 200°C.; CO molecules consumed $=1.98\times10^{18}$, Ni atoms of film $=2.9\times10^{19}$. (c) After reaction at 250°C.; CO molecules consumed $=1.29\times10^{19}$, Ni atoms of film $=3\times10^{19}$.

It has been pointed out by several authors[12,13,14] that in the carburization of nickel by carbon monoxide, carbide is initially formed and then graphitic carbon is produced, which increases with the rise in reaction temperature[15]. When the extent of decomposition is small no pattern of nickel carbide is detected. This fact may be interpreted as the insufficient intensity of diffraction by carbide of a small amount, even though it exists. We can conclude, therefore, that carbon monoxide is converted to carbon dioxide and nickel carbide instead of graphitic carbon on the surface of evaporated nickel films under our experimental conditions.

Discussion

As has been mentioned in part 1, the surface is assumed to be non-uniform and consisted of two areas A and B with different activity. From the fact that the decomposition at high temperatures occurs after the initial rapid adsorption which covers a fraction of surface similar to that at *room-temperature-adsorption*, it is surely expected that carbon monoxide molecules adsorbed on B would participate in the reaction. Furthermore, the fact that the heat of adsorption obtained from the temperature dependency of b is smaller than that on A (=35 kcal/mol.) also suggests that the molecules adsorbed on B with lower heat of adsorption would be activated and undergo decomposition. That is, in the decomposition of carbon monoxide, sites with high heat of adsorption are not active but those with low heat are rather active because of the ease of desorption. Similar observation has been made by Beeck[16] in the catalytic hydrogenation of ethylene with various evaporated metallic films. He has pointed out that the metals with higher activity possess lower heat of adsorption for ethylene and explained this finding by the reasoning that metals with higher heat of adsorption for ethylene are poisoned more seriously by adsorbed ethylene and its degradation products because of the difficulty of desorption.

In the previous investigations[7,17] on the decomposition of carbon monoxide by reduced nickel catalysts, such a phenomenon as that rapid adsorption precedes decomposition has not been observed. This difference may be attributed to the difference in the cleanliness of the surface. That is, under any conditions for the preparation of reduced catalysts generally adopted, it seems to be very difficult or impossible to drive out some impure gases which adhere firmly to the surface and produce such a clean surface as evaporated film. The catalytic reactions on these reduced catalysts have been well interpreted in terms of the intrinsic heterogeneity of the surface. In this work also, to explain the results obtained, it has been necessary to assume the surface heterogeneity on the evaporated nickel films, in spite of their cleanliness. However, it is uncertain whether this heterogeneity is due to the intrinsic difference in surface energy or the interaction of adsorbed molecules or both.

In conclusion, the author wishes to express his thanks to Messrs. Y. Mizushima and T. Ichimiya for their interest in this investigation and for valuable discussion; to Mr. K. Ono for the electron diffraction study, and to Mr. K. Nakagawa for mass-spectrometric analysis.

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

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

[14] S. Oketani, S. Nagakura and K. Tsuchiya, *J. Japan Inst. Metals*, **18**, 325, 329 (1954).

[15] The critical temperature where the process $Ni_3C\rightarrow C+Ni$ (or Ni_xC) begins to occur has been variously reported, for example 270,[12] 420 [13] or 500°C[14].

[16] O. Beeck, *Disc. Farad. Soc.*, No 8, 118 (1950).

[17] T. Kwan and T. Izu, *Catalyst*, No 6, 43 (1949).