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Hydrogenation of Nitrogen Chemisorbed in Different States on an Iron Synthetic Ammonia Catalyst*

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The hydrogenation of adsorbed nitrogen was carried out on a well-reduced iron synthetic ammonia catalyst. The rate of the hydrogenation strongly depended upon the temperature of the adsorption when the hydrogenation was carried out at a given temperature of the hydrogenation, amount of adsorbed nitrogen and a given partial pressure of hydrogen. It was concluded that at least two types of chemisorbed nitrogen exist on the catalyst in accordance with our previous results (*1*): one of them is stable near 200°C, whereas the other exists predominantly above 400°C.

The kinetics of the hydrogenation of both types of adsorbed nitrogen was studied and its mechanism was discussed in connection with that of the ammonia synthesis reaction. In addition, the isotope effect of hydrogen was also studied.

INTRODUCTION

The states of chemisorbed nitrogen were previously investigated on the iron synthetic ammonia catalyst (*1*) in which the effect of chemisorbed nitrogen upon the carbon monoxide adsorption was studied. It was found that preadsorbed nitrogen produced effect upon the carbon monoxide adsorption and the effect changed with the temperature of nitrogen adsorption. From the work, the conclusion was drawn that nitrogen chemisorbed in two different states, depending upon the temperature, i.e., one of them predominantly exists in molecular $\mathrm{N{\equiv}N{-}}$ or undissociative $\underset{/\!\!/}{\mathrm{N}}{-}\underset{\backslash\!\!\backslash}{\mathrm{N}}$ or $\underset{/}{\mathrm{N}}{=}\underset{\backslash}{\mathrm{N}}$ form near 200°C, whereas above 400°C it is in dissociative form $\mathrm{N{\equiv}}$. Later, the experiments of the hydrogenation of nitrogen preadsorbed at different temperatures were carried out (*2*) and the rate was found to be strongly affected by the temperature of the adsorption, confirming the above results (*1*).

In this connection, we aimed to elucidate the mechanism of the hydrogenation of both types of chemisorbed nitrogen.

EXPERIMENTAL

An iron synthetic ammonia catalyst (2.6 g, 2.03% alumina, 0.81% potassium oxide and 0.16% silica as promoters) was reduced in a stream of hydrogen at a flow rate of 500 $\mathrm{cm^3}$ STP/min for 45 hr and 40 hr at the respective temperatures of 450 and 600°C in Series I experiments. Prior to Series II experiments, the catalyst used in Series I experiments was oxidized in air and reduced again at 600°C for 50 hr.

At the end of the reduction, the catalyst was degassed at 600°C for 3 hr to 2×10^{-6} mm Hg. Nitrogen was adsorbed either near 210 or 440°C, and at pressures of 20–120 mm Hg. The amount of adsorbed nitrogen was varied by changing time of the adsorption or the pressure of nitrogen. After nitrogen had been adsorbed, the temperature was lowered to that for hydrogenation and nitrogen in the gas phase was removed by a Toepler pump. The amount

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* The present work was communicated in part in N. Takezawa, *J. Phys. Chem.* **70**, 597 (1966).

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of nitrogen adsorbed during the process of decreasing temperature was less than 0.15 cm^3 STP.* Thereafter, hydrogen or the mixtures of hydrogen and helium at a total flow rate of 453 cm^3 STP per min was passed over the catalyst on which nitrogen had been adsorbed. Helium was used as a diluent in order to vary the partial pressure of hydrogen. All hydrogenation experiments were carried out at total pressure of 1 atm. In some experiments, deuterium was used instead of hydrogen.

The amount of ammonia thus formed was successively followed by absorption in sulfuric acid solution. Between the runs, the catalyst was reduced at 450 and 600°C for 2 and 12 hr, respectively.

Nitrogen was purified by passage through heated copper (450°), heated nickel (450°), soda lime, potassium hydroxide, and reduced iron (500°) and finally through a trap immersed in liquid nitrogen. Hydrogen or deuterium was carefully purified by passage through palladium-silver alloy thimble and a trap immersed in liquid nitrogen.

RESULTS

When the hydrogen stream is passed over the catalyst with preadsorbed nitrogen, the nitrogen readily hydrogenated into ammonia. Figure 1 shows examples of the plot of the amount of ammonia thus formed against time of the hydrogenation.

The results of Series I experiments are shown in Fig. 2 in which the outflow rate n_t of ammonia is plotted against the amount v of preadsorbed nitrogen. The outflow is always estimated from the initial slope of the curve as illustrated in Fig. 1.†

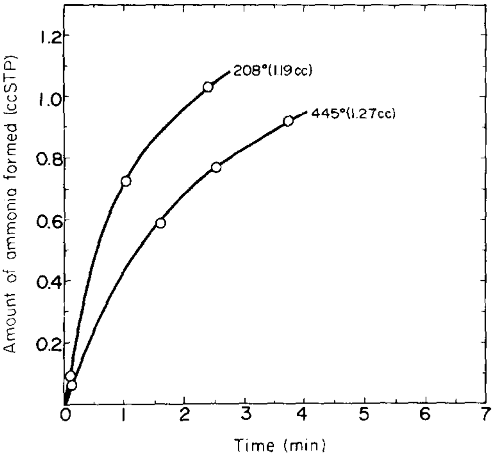

FIG. 1. Ammonia formation from the hydrogenation of adsorbed nitrogen at 208°C. Temperature in the figure represents that of the nitrogen adsorption. The numbers in the brackets represent the amount of preadsorbed nitrogen.

From Fig. 2, n_t is expressed at a constant partial pressure of hydrogen as‡

$$n_t = k_1 \exp(hv), \qquad (1)$$

where h and k_1 are constants at given temperatures of the hydrogenation and the nitrogen adsorption.§ It is further evident from the figure that nitrogen chemisorbed near 210°C (hereinafter referred to as L-type nitrogen) is more reactive compared with that chemisorbed near 440°C (H-type nitrogen). This is, therefore, compatible

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* This additional amount of nitrogen was mostly adsorbed above 380°C, since the rate of the adsorption is extremely small at lower temperatures. Since H-type nitrogen exists predominantly even at 380°C (*1*), this could be H-type nitrogen.

† In the present experiments, apparent volume of the catalyst bed is about 0.7 cm^3. Therefore, hydrogen flows through it within 0.03 sec if the free space is assumed to be about one third of the apparent volume as is usually used. It can be, therefore, safely assume that the flow readily become steady. It can be also estimated that only 0.0002 cm^3 STP of nitrogen is hydrogenated during this period. The errors of n_t are within 5% at largest.

‡ Hydrogen stream through the catalyst with preadsorbed nitrogen was passed over molecular sieve 5 Å (immersed in liquid nitrogen) for time sufficient to consume about a half of adsorbed nitrogen as ammonia at 208°C. Gases collected on molecular sieve was mass spectrometrically analyzed and no gaseous nitrogen was detected. Therefore, preadsorbed nitrogen was mostly consumed as ammonia.

§ In the present experiments, the adsorption is always carried out for time shorter than 2 hr. The outflow is found to be independent of time of the nitrogen adsorption. In this respect, the effect of the time can be neglected in the present discussion.

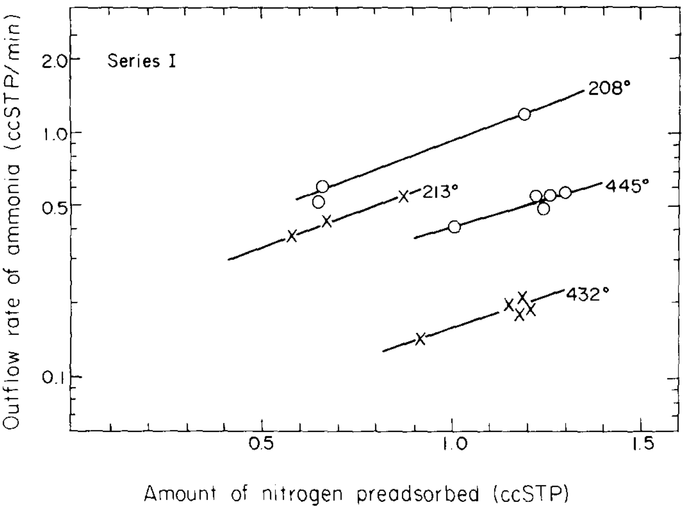

FIG. 2. Plot of the outflow rate of ammonia against the amount of preadsorbed nitrogen (Series I). Hydrogenation temperature: 208°(○) and 162°(X). Flow rate of hydrogen: 453 cm^3 STP per min. Partial pressure of hydrogen: 1 atm. Temperature of the nitrogen adsorption is shown in the figure.

with our previous results (*1*) in which two types of chemisorbed nitrogen were suggested, i.e., one predominantly exists near 200°C and the other above 400°C. Similar results are obtained from Series II experiments.

Figure 3 shows the plot of the reciprocal of the flow rate N_H of hydrogen against the outflow rate n_t of ammonia. The outflow is practically independent of the flow rate of hydrogen when *H*-type nitrogen is hydrogenated at 162°C. The hydrogenation of *L*-type nitrogen, however, strongly depends

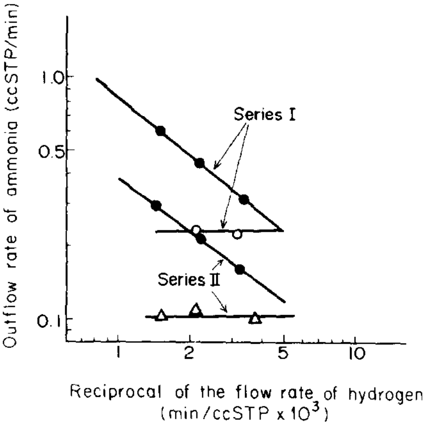

FIG. 3. The relation between the flow rate of hydrogen and the outflow rate of ammonia. Hydrogenation of *L*-type nitrogen: At 208°(●) (Series I); amount of preadsorbed nitrogen, 0.68–0.71 cm^3 STP. At 162°(●) (Series II); amount of preadsorbed nitrogen, 0.53–0.55 cm^3 STP. Hydrogenation of *H*-type nitrogen: At 162°(○) (Series I); amount of preadsorbed nitrogen, 1.26–1.29 cm^3 STP. At 162°(△) (Series II); amount of preadsorbed nitrogen, 0.83–0.86 cm^3 STP.

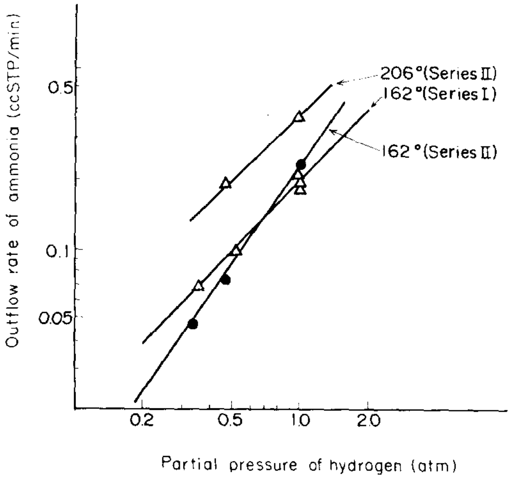

FIG. 4. The effect of the partial pressure of hydrogen upon the outflow rate of ammonia. Hydrogenation of *L*-type nitrogen (●) (Series II); amount of preadsorbed nitrogen 0.56–0.62 cm^3 STP. Hydrogenation of *H*-type nitrogen (△) (Series I and II); amount of preadsorbed nitrogen, 1.16–1.23 cm^3 STP (Series I) and 0.97–0.99 cm^3 STP (Series II). Temperatures in the figure represent that of the hydrogenation.

upon the flow rate of hydrogen at 208 and 162°C. The outflow n_t is proportional to $(1/N_H)^{-0.75}$.

Figure 4 shows the effect of the partial pressure P_H of hydrogen upon the ammonia formation. The outflow is found to be proportional to $P_H^{0.95}$ when H-type nitrogen is hydrogenated, whereas the hydrogenation of L-type nitrogen proceeds in proportion to $P_H^{1.35}$.

The adsorbed nitrogen is hydrogenated with deuterium in order to examine the isotope effect of hydrogen upon the formation of ammonia. The formation of deuteroammonia from H-type nitrogen is slower than that of normal ammonia. The ratio of the outflow rate n_t^D of deuteroammonia to that n_t of normal ammonia is about 0.8 at 162°C. However, the effect is reverse in the deuteration of L-type nitrogen. The ratio n_t^D/n_t is about 1.35 at the same temperature.

DISCUSSION

I. The Estimation of the Rate of the Hydrogenation of Adsorbed Nitrogen

A flow balance at the outlet of the catalyst bed yields the following equation

$$V = dx_t/d(1/N_H),^* \qquad (2)$$

where V represents the rate of the hydrogenation allotted for entire volume of the catalyst bed. The x_t is the mole fraction of ammonia at the outlet. Inflow rate of hydrogen N_H may be used for outflow, since n_t is at largest 0.3% of N_H. The x_t can be, therefore, approximated as

$$x_t = n_t/N_H. \qquad (3)$$

Therefore, (2) can be rewritten as

$$V = n_t + (1/N_H)[dn_t/d(1/N_H)], \qquad (4)$$

With the aid of the dependence of n_t upon $1/N_H$ in Fig. 3 (see previous section), (4) can be written as

$$V = n_t \qquad (5)$$

and

$$V = n_t/4, \qquad (6)$$

respectively, for the hydrogenation of H- and L-type nitrogen.

II. The Effect of Ammonia

The effect of ammonia upon the rate V is determined from the experiments in which the flow rate of hydrogen and the amount of adsorbed nitrogen are held constant.

The results in Fig. 3 are replotted in Fig. 5 in which the rate V is shown as a function of the partial pressure of ammonia P_A. The P_A is identical with the mole fraction x_t of ammonia since the hydrogenation is carried out under atmospheric pressure. It is, therefore, evident that the hydrogenation of H-type nitrogen proceeds independently of the partial pressure of ammonia but that of L-type nitrogen is retarded in the presence of ammonia.

The ratio of the forward rate V_+ to the backward V_- of the reaction $\Sigma_i l_i L_i = \Sigma_i r_i R_i$ is generally given (*3*), if the rate-determining step exists, as

$$V_-/V_+ = \exp(\mu^R - \mu^L/\nu_r RT), \qquad (7)$$

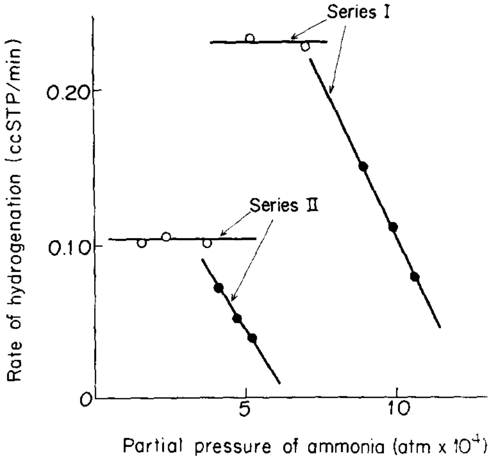

FIG. 5. Plot of the rate of the hydrogenation against the partial pressure of ammonia. Hydrogenation of L-type nitrogen (○) at 208° (Series I) and at 162° (Series II). Hydrogenation of H-type nitrogen at 162° (○) (Series I and II). Partial pressure of hydrogen: 1 atm. Amount of preadsorbed nitrogen: see Fig. 3.

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* When the hydrogen stream is diluted with helium, N_H in (2) is substituted for the total inflow, i.e., the sum of the inflow rates of hydrogen and helium.

where μ^L or μ^R is the sum of the chemical potentials of L_i or R_i and ν_r is the stoichiometric number of the rate-determining step. If the hydrogenation occurs preferentially as

$$2N(a) + 3H_2 = 2NH_3 \qquad (8)$$

or

$$N_2(a) + 3H_2 = 2NH_3, \qquad (9)$$

(7) can be rewritten as

$$V_-/V_+ = A(P_A^2/P_H^3)^{1/\nu_r}, \qquad (10)$$

respectively, for those cases. In (10), $A = \exp(2\mu_A^0 - 3\mu_H^0 - \mu_{Na}/\nu_r RT)$. μ_{Na} is the chemical potential of adsorbed nitrogen $N_2(a)$ or twice that of $N(a)$ and, μ_A^0 and μ_H^0 are those of ammonia and hydrogen at a standard state, respectively.

Since the rate V of the overall process is expressed as the difference between V_+ and V_-, i.e., $V = V_+ - V_-$, (10) can be rewritten as

$$V = V_+[1 - A(P_A^2/P_H^3)^{1/\nu_r}]. \qquad (11)$$

Therefore, the rate V is influenced by the presence of ammonia, if the backward reaction occurs appreciably. In this respect, it is concluded that in the hydrogenation of H-type nitrogen the backward reaction is negligible and the forward rate is unaffected by the partial pressure of ammonia. The rate can be practically given as

$$V = V_+ = n_t = k_1 \exp(hv) \qquad (12)$$

in accordance with (1) and (5).

On the other hand, L-type nitrogen is hydrogenated in different manner. On the assumption that the forward reaction is unaffected by ammonia as in (12), the effect of ammonia can be interpreted in terms of the occurrence of the backward reaction, i.e., the rate can be written as

$$V = n_t/4 = k_2 \exp(h'v)[1 - A(P_A^2/P_H^3)^{1/\nu_r}] \qquad (13)$$

in accordance with (6) and (11), where k_2 and h' are constants corresponding to k_1 and h in (12), respectively. The rate V is plotted against the partial pressure of ammonia P_A or its square P_A^2, and it is found that both V and P_A or V and P_A^2 bear good relationships for $\nu_r = 2$ or 1 from the present experiments.

III. The Effect of Hydrogen

As Fig. 4 shows, hydrogen markedly influences the rate of the hydrogenation. If only k_1 is affected by the partial pressure of hydrogen, the rate of the hydrogenation of H-type nitrogen is given by reference to (12) as

$$V = V_+ = k_H P_H^{0.95} \exp(hv), \qquad (14)$$

where $k_1 = k_H P_H^{0.95}$ and k_H is constant.

Since the backward reaction occurs appreciably in the hydrogenation of L-type nitrogen, the effect of hydrogen is not determined directly from Fig. 4. On the assumption that (6) is valid at any pressure of hydrogen employed, the forward rate $k_2 \exp(h'v)$ (in (13)) at a given amount of adsorbed nitrogen is estimated from the plots P_A vs $n_t/4$ or P_A^2 vs $n_t/4$. As (14) is obtained, (13) can be, therefore, given as

$$V = k_L P_H^{1.04} \exp(h'v)[1 - A(P_A/P_H^{1.5})] \qquad (\nu_r = 2) \quad (15)$$

or

$$V = k_L P_H^{1.08} \exp(h'v)[1 - A(P_A^2/P_H^3)], \qquad (\nu_r = 1) \quad (16)$$

where $k_2 = k_L P_H^{1.04}$ or $k_L P_H^{1.08}$ and k_L is constant.

From the temperature dependence of the forward rate V_+ of the hydrogenation of H-type nitrogen, the activation energy is estimated to be about 12 kcal/mole. The value for the hydrogenation of L-type nitrogen is not estimated since we do not have sufficient data to estimate the forward rate at various temperatures.

IV. The Mechanism of the Hydrogenation

It was previously concluded (*4–6*) that the ammonia decomposition over the doubly promoted iron catalyst is controlled by the desorption of adsorbed nitrogen near 400°C, whereas with the rise of the temperature the dehydrogenation of adsorbed amino $NH_2(a)$ controls the rate on the assumption that the decomposition proceeds through the scheme as

$$NH_3 = NH_2(a) + H(a), \qquad (17a)$$
$$NH_2(a) = NH(a) + H(a), \qquad (17b)$$
$$NH(a) = N(a) + H(a) \qquad (17c)$$
$$2N(a) = N_2 \qquad (17d)$$

and

$$2H(a) = H_2. \qquad (17e)$$

In this respect, the hydrogenation (8) is assumed to be composed of the reverse steps of (17a), (17b), (17c) and (17e).[*] The formation of adsorbed amino, i.e., the reverse of (17b), appears to be the slowest step in these four steps.[**]

The rate of the reaction is formulated (*3, 7*) allowing for the repulsive interaction among adsorbed species inclusive of the critical complexes of the rate-determining step by proportional approximation. The formation of adsorbed amino can be followed by the reaction kinetics as

$$V_+ = k_3(1 - \theta)P_H \exp(hv), \qquad (18)$$

where k_3 is constant and θ the surface covered with adsorbed nitrogen. This fairly accords with (14).[†]

In similar manner, (15) or (16) can be obtained by considering the backward reaction. However, if *L*-type nitrogen is in molecular $\mathrm{N{\equiv}N{-}}$ or undissociative $\underset{/\!/\qquad\backslash\!\backslash}{\mathrm{N{-}N}}$ or $\underset{/\qquad\backslash}{\mathrm{N{=}N}}$ form, (9) is the overall process. In this case, the formation of diimide $N_2(a) + H_2 = N_2H_2(a)$ may be rate-determining if (9) is composed of the steps as was proposed by Mars *et al.* (*8*).

The ratio of A (in (13)) for the normal ammonia formation (8) or (9) to A^D for the deuteroammonia is theoretically (*3, 7*) estimated to be $1/\nu_r$ power of that of equilibrium constant K of the normal ammonia synthesis $N_2 + 3H_2 = 2NH_3$ to the constant K^D of the deuteroammonia synthesis, i.e., $A/A^D = (K/K^D)^{1/\nu_r}$.

Since the ratio K/K^D is actually 0.0114 at 162°C (*9*), the A/A^D-value should be 0.107 and 0.0114 for $\nu_r = 2$ and 1, respectively. With the aid of A-value experimentally obtained from (15) or (16), it can be concluded that the backward reaction is practically negligible in the deuteration of *L*-type nitrogen, regardless ν_r-value. Similarly, it is also negligible in the deuteration of *H*-type nitrogen since in its hydrogenation A-value is very small (no backward reaction). In these respects, the forward rate V_+^D of the deuteration of both *L*- and *H*-type nitrogen is practically equal to n_t^D as in the hydrogenation of *H*-type nitrogen. The ratio of V_+^D to the forward rate V_+ of normal ammonia formation is 0.8 in the hydrogenation of *H*-type nitrogen, since $V_+^D/V_+ = n_t^D/n_t$. However, in the hydrogenation of *L*-type nitrogen, V_+^D/V_+-value is not approximated by n_t^D/n_t-value because the backward reaction occurred appreciably in the normal ammonia formation. Considering the effect of the backward reaction, we can estimate V_+ from (15) or (16) and have $V_+^D/V_+ =$ 1.35 and 2.0 for $\nu_r = 2$ and 1, respectively. These results, therefore, suggest that *L*-type nitrogen is hydrogenated through a mechanism different from that of the hydrogenation of *H*-type nitrogen.

V. *Relevance to other Work*

Tamaru (*10*) previously studied the hydrogenation of nitrogen adsorbed on the doubly promoted iron catalyst in connection with the mechanism of the ammonia synthesis. It was found that the hydrogenation was proportional to $P_H \exp(hv)$ and deuteroammonia was formed faster than normal ammonia. Aika and Ozaki

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[*] The stoichiometric numbers of each steps are 2, 2, 2 and 3, respectively.

[**] The adsorption of hydrogen during the hydrogenation is found to be immeasurably rapid at 208°C and a pressure of hydrogen at 1 atm. Even at the pressure of 7.6 cm Hg of hydrogen, the rate at 208°C is faster than 3 cm³ STP per min (0.66 cm³ STP of nitrogen was preadsorbed). Therefore, the hydrogen adsorption proceeds extremely fast compared to the hydrogenation.

[†] Similar equation can be also obtained for this mechanism on the alternative assumption that the surface is heterogeneous, i.e., particular assumptions are made on the distributions of the adsorption energies and of the energies of the critical complex of the rate-determining step (so-called heterogeneous model) instead of the interactions introduced in the present discussion (homogeneous model).

(11), however, recently pointed out from the replot of Tamaru's results that the hydrogenation proceeded in proportion to the 1.5th power with respect to the partial pressure of hydrogen but not to the first power. From these results, these authors suggested that the hydrogenation was actually in equilibrium with respect to the reaction (8). The isotope effect was, therefore, interpreted on the above basis.

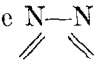
It should be noted, however, from Tamaru's results that the ratios n_t^D/n_t at 180, 250, and 320°C are 2.9, 3.7, and 4.2, respectively. If (8) or (9) attains equilibrium at these temperatures, the ratio n_t^D/n_t should be decreased with the rise of the temperature *(9)*. Therefore, the above suggestion seems not to be consistent with these observations.

These results suggest, however, that in Tamaru's experiments *L*-type nitrogen preferentially participates in the hydrogenation, although the activity of the catalyst used by Tamaru is much less active compared with that of the present catalyst.*

VI. The States of Adsorbed Nitrogen

It was found previously that *H*-type nitrogen produced no effect upon the adsorption of carbon monoxide, but *L*-type nitrogen inhibited it. In the present work, the difference between *H*- and *L*-type nitrogen is again clearly demonstrated from the hydrogenation.

According to the work on the hydrogenation of iron nitride *(12, 13)*, it was found that the reaction proceeded in the first power with respect to the partial pressure of hydrogen with the activation energy of 12–15 kcal/mole. These results accord excellently with the present results obtained in the hydrogenation of *H*-type nitrogen, suggesting that *H*-type nitrogen is in a structure similar to nitride. Possibly, it is located among surface iron atoms as surface nitride** in dissociative form. However, no evidences are obtained as to the structure of *L*-type nitrogen. It may be in molecular $N{\equiv}N{-}$ or undissociative $N{-}N$ or $N{=}N$ form as suggested in the previous work *(1)*.



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* The activity of the present catalyst at 208°C is found to be about 4000 times that of the catalyst used by Tamaru at 250°C as to the nitrogen adsorption at given surface coverage of nitrogen. The difference in the activities is not given, however, for the hydrogenation of adsorbed nitrogen, since the backward reaction can not be evaluated from Tamaru's results.

** The formation of iron nitride and the absorption of nitrogen in bulk are not feasible under the present experimental conditions *(1)*.