Mechanism and Isotope Effect in Ammonia Synthesis over Molybdenum Nitride

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The mechanism of ammonia synthesis over molybdenum nitride has been studied by means of ^{15}N tracer, deuterium isotope effect, and kinetics. The kinetic data as well as the deuterium isotope effect indicates that the rate-determining step is the chemisorption of nitrogen retarded by adsorbed nitrogen atoms, which is the same situation as concluded with the unpromoted iron. In agreement with this conclusion, it is found that no isotopic mixing takes place in the reactant nitrogen during the synthesis. The subsequent step of the synthesis, i.e., the hydrogenation of the adsorbed nitrogen, is evidently equilibrated. The deuterium isotope effect in the rate of hydrogenation of preadsorbed nitrogen is caused thermodynamically.

INTRODUCTION

It is generally accepted that the most important process in ammonia synthesis is the activation of nitrogen molecule. This has been reflected on the rate-determining step of the reaction which is accepted to lie in the step of dissociative adsorption of nitrogen as proved for iron catalysts (1). On the other hand, it has been suggested that nitrogen is readily adsorbed dissociatively over those metals which have a strong affinity to nitrogen, so that the rate-determining step shifts to the surface hydrogenation of the adsorbed nitrogen (2).

Hill, Kemball, and Roberts (3) (H.K.R.) recently reported the following: (a) A sample of reduced molybdenum dioxide readily absorbed nitrogen forming a nitride phase; (b) the rate of absorption was faster than that of hydrogenation of the nitride; and (c) the synthesis reaction continued with unchanged rate for a period after the removal of gas phase nitrogen. On the basis of these results, they concluded that the rate of ammonia synthesis was controlled by one of the steps in the conversion of adsorbed nitrogen to ammonia and not by the chemisorption of nitrogen.

If their conclusion is accepted, a normal deuterium isotope effect in ammonia synthesis should be observed on molybdenum nitride catalyst, in contrast to iron catalyst on which deuterium reacts faster than hydrogen with nitrogen (4, 5). The isotope effect study for the case where the reaction mechanism is different from that on iron catalyst must give a new approach to the problems of mechanism and isotope effect. This prediction constitutes the initial object of the present study. Preliminary work was devoted to examination of the behaviors of catalyst sample in reduction and nitridation, reexamining the results of H.K.R. (3). The mechanism of the synthesis was investigated by means of ^{15}N tracer as well as the isotope effect and kinetics.

EXPERIMENTAL

The apparatus was a conventional circulating system with traps and was used for reduction and nitridation of catalyst and for the synthesis runs. Adsorption measurement was also possible by this ap-

paratus. The reaction vessel was made of Pyrex glass. Three liquid-nitrogen traps were used in the synthesis run to ensure the condensation of ammonia. The circulation of gas was performed by means of a glass piston pump, and the flow rate was measured and controlled by an orifice meter calibrated at ambient pressures.

The variation of isotopic concentration in hydrogen, nitrogen, or ammonia was measured by intermittent sampling. The isotopic analyses were made by a Mass Filter type mass spectrometer.

Cylinder hydrogen used for reduction and hydrogenation was purified by passing over a platinum-asbestos catalyst at 350°C followed by drying at —78°C. Nitrogen in cylinder was dried in a similar manner and freed from oxygen by passing over a copper-Kieselguhr unit at 200°C. The synthesis gas was prepared by decomposition of ammonia or deutero-ammonia on a ruthenium catalyst at 430°C. Atomic D concentration of the deuterium thus obtained was 95%.

Heavy nitrogen gas was prepared as follows. Ammonium sulfate containing 70% ^{15}N that was obtained from the Institute of Physical and Chemical Research was decomposed in calcium hydroxide solution to ammonia, which was oxidized to nitrogen by cupric oxide. The nitrogen gas rich in ^{15}N was mixed with $^{28}N_2$. The sample of molybdenum trioxide (99% purity) was supplied by Wako Pure Chemical Industry Ltd., and was pressed into a pellet form.

RESULT

Reduction of Molybdenum Trioxide and Nitridation

There are some discrepancies in the reported behavior of molybdenum oxide during reduction (3, 6, 7) and in the reported reactivity of molybdenum metal with nitrogen (3, 8). It would be better to examine the properties of the sample first. Molybdenum trioxide (5.09 g) was reduced by circulating hydrogen of a flow rate of about 150 ml/min at 492°C, and the water formed was trapped at —78°C. The rate

of reduction was appreciable already at 400°C, but too slow to perform the reduction (0.2% for 1.5 hr), whereas it was rapid at 492°C. The hydrogen gas for the reduction was supplied intermittently so that the hydrogen pressure during reduction varied in a range from 400 to 600 mm Hg. Meanwhile, the integrated amount of hydrogen consumption was recorded.

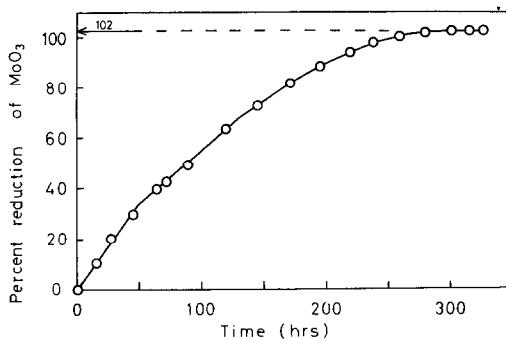The time course of reduction is shown in Fig. 1. The extent of reduction of MoO_3

FIG. 1. Time course of the reduction of molybdenum trioxide. P_{H2}, 500 mmHg; Flow rate, 150 ml/min; Temp., 492 ± 3°C; Original weight, MoO_3 = 5.09 g.

on the longitudinal axis is estimated from the hydrogen consumption assuming stoichiometric MoO_3. It may be seen from this figure that the initial constant rate of reduction was slowed down after 33%, resulting another region of constant rate. This change in the rate of reduction seems to reflect the phase change from MoO_3 to MoO_2 at 33%.* The second region of constant rate is likely to come to end at 67% where the reduction of MoO_2 to MoO is expected to be over. The subsequent stage of the reduction proceeded with a diminishing rate. Thus it took 280 hr before no hydrogen consumption was detected, while 50 hr of hydrogen treatment was made in addition. The total consumption of hydrogen agrees fairly well with the value expected for complete reduction of MoO_3.

Measurement of surface area of the

* According to Funaki and Ogawa (9), MoO_2 is stable during the reduction of MoO_3.

catalyst was made several times in the course of the reduction by BET method using nitrogen. The result is shown in Table 1. It is clear that the surface area increases with the extent of reduction. The final value of surface area is seven times as large as that of MoO_2 state, while H.K.R. reported a fifty-fold increase in the same region.

TABLE 1
BET SURFACE AREA IN THE COURSE OF THE REDUCTION OF MoO_3

Reduction percentage	0	31	73	100
Surface area (m^2/g Mo)	0.53	0.83	4.5	5.3

When the reactant gas ($N_2 + 3H_2$) was introduced over the metallic molybdenum, the formation of nitride phase was suggested on the basis of the nitrogen balance, and thus the stationary rate of reaction could not be observed. Since the isotope effect should be examined under a stationary and reproducible condition, it was decided to work on a preformed nitride.

Although Ghosh (8) reported that no nitride was formed from nitrogen and molybdenum metal at 400–1000°C, H.K.R. reported that the completely reduced molybdenum absorbed nitrogen even at 200°C. The reduced molybdenum used in this study was found to absorb nitrogen very slowly below 400°C, but fairly fast around 500°C. The time course of nitridation at 502°C with an initial pressure of 795 mm Hg is shown in Fig. 2. The fairly high rate of nitridation in the initial stage decreased as the nitridation proceeded. After a 69 hr of nitridation with nitrogen, during which about 146 ml(STP)/3.39 g Mo of nitrogen was absorbed, the nitrogen was replaced by the synthesis gas mixture of 150 mm Hg which was circulated with a trap cooled at −78°C. It is shown in Fig. 2 that the replacement enhanced the absorption of nitrogen (dotted line), which must be due to the presence of hydrogen. The action of hydrogen may be explained in two ways. First, the hydrogen might remove a trace amount of impurity such as
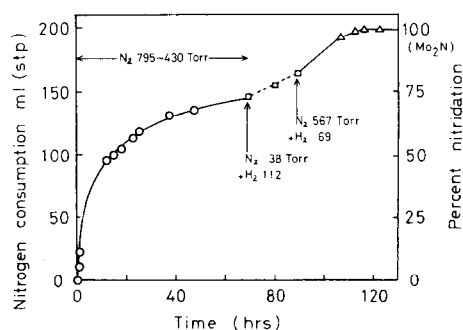

FIG. 2. Time course of nitridation of molybdenum metal. Temp., 502 ± 2°C.

oxygen because a minute amount of condensate was detected in the trap. Second, the hydrogen might take part in the dissociation of nitrogen because an enhanced adsorption of nitrogen in the presence of adsorbed hydrogen was observed by H.K.R. After 120 hr, the nitrogen absorption was over, resulting in a nitride, Mo_2N, which was a grey color. It was identified as $Mo_2N(\gamma)$ by means of X-ray diffraction. The BET area of the nitride was measured to be 13.5 m^2/g Mo.

Ammonia Synthesis

The steady rate of ammonia synthesis was readily obtained on the molybdenum nitride. The reaction rate gave a quick response to the variation of conditions such as temperature, total pressure, and flow rate of gas, and it was found to be reproducible. Thus, when the reactant gas ($N_2 + 3H_2$) was circulated through the catalyst bed under a fixed condition of a constant total pressure (P atm) and a constant flow rate (q liters(STP)/hr), a constant concentration of ammonia (y) could be expected at the exit of catalyst bed, while this was subsequently trapped at −195°C. Since the rate of ammonia synthesis is half the rate of decrease in the reactant (V liters(STP)/hr), the following relationship is obtained:

$$y = \frac{V}{2q}.$$

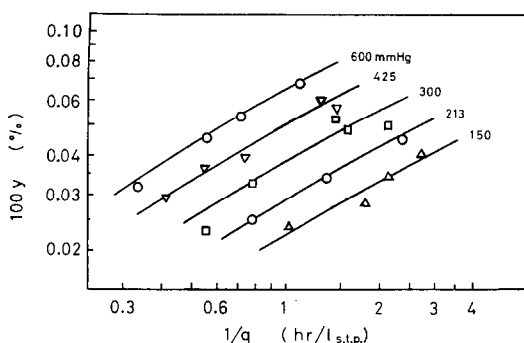The rate measurements at 235–355°C showed that the higher the flow rate, the higher the observed rate, and that the

Fig. 3. Kinetic results in hydrogen system ($N_2 +$ $3H_2$) at 330°C. Relation between ammonia concentration (y), flow rate (q), and total pressure (mm Hg). Solid lines are drawn by Eq. (15).

deuterium system reacted about 1.6 times faster than hydrogen at 330°C, contrary to the early expectation. The dependencies of the reaction rate on total pressure, flow rate, and hydrogen isotope were examined at 330°C. The results of these experiments are shown as a relationship between log y and log ($1/q$) in Figs. 3 and 4.

From the principle of flow reactor the reaction rate r (l_{NH3}/hr/g cat) is obtained as follows:

$$r = \frac{1}{W}\frac{dy}{d(1/q)},\qquad(1)$$

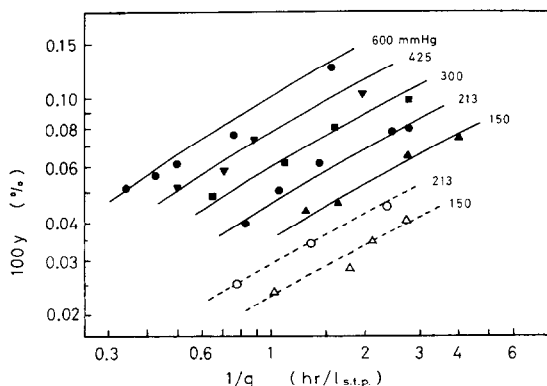where W is catalyst weight (g). Figures 3 and 4 suggest that there can be a linear

Fig. 4. Kinetic results in deuterium system ($N_2 + 3D_2$) compared with hydrogen system (white circles) at 330°C. Relation between ammonia concentration (y), flow rate (q), and total pressure (mm Hg). Solid lines are drawn by Eq. (15).

relationship between log y and log ($1/q$) as follows:

$$n \log y = \log c - \log q.\qquad(2)$$

The experimental rate equation is obtained from Eqs. (1) and (2) are as follows:

$$R = \frac{c}{n}y^{(1-n)},\qquad(3)$$

where $R = rW$.

The data at 330°C is adjusted to Eq. (3), and the rate equations are obtained as follows:

$$R_H = 1.09$$
$$\times\ 10^{-6}P^{1.43}y^{-0.82}(\text{liters(STP)}NH_3/\text{hr})\quad(4)$$

for hydrogen system, and

$$R_D = 0.77$$
$$\times\ 10^{-6}P^{1.22}y^{-0.95}(\text{liters(STP)}ND_3/\text{hr})\quad(5)$$

for deuterium system, with total pressure P (atm).

Apparent temperature dependency of synthesis rate was examined under the condition of constant pressure and flow rate. The results are shown in Fig. 5. The reaction rate at 235°C was so low that no reliable data could be obtained. From Fig. 5 apparent activation energies are obtained to be 12.4 kcal/mole for hydrogen system and 13.2 kcal/mole for deuterium system. These values are in fairly good agreement with 14 kcal/mole reported by H.K.R. (3).

The reaction rate under the same condition as employed by H.K.R. can be estimated by Eq. (4) to be 3.4 ml/hr/g Mo or 0.25 ml/hr/m² at 500°C, while H.K.R. gave a value of 0.15 ml/hr/m².

In order to examine the rate-determining step of the ammonia synthesis, nitrogen-15 tracer was adopted. In this experiment ordinary reactant gases ([28]$N_2 + 3H_2$) were evacuated at the reaction temperature for 1 min to 1 mm Hg, and replaced by the gas mixture ($N_2 + 3H_2$) containing [30]N_2 28.9%, [29]N_2 26.6% and [28]N_2 44.5%. In the course of the synthesis reaction, isotopic distributions in nitrogen and ammonia were measured by seventeen and six samplings,
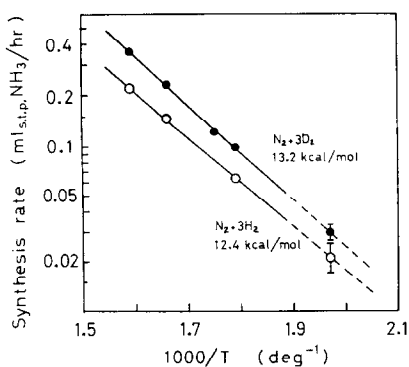
Fig. 6. Time course of extent of reaction and of ^{15}N concentration in ammonia produced from ^{15}N–42.2% nitrogen. Temp., 330°C.

respectively. In a period of 122 hr, the total pressure of the closed system (about 400 ml) decreased from 428 to 92 mm Hg partly because of the samplings.

The time course of the extent of reaction is shown in Fig. 6 together with the variation of ^{15}N concentration in ammonia.* The isotopic composition of nitrogen (^{30}N$_2$, ^{29}N$_2$, and ^{28}N$_2$) remained at the initial value with ±0.2% deviation. This indicates that no isotopic mixing in nitrogen (^{30}N$_2$ + ^{28}N$_2$ → 2^{29}N$_2$) occurred appreciably during the period under the reaction condition.

It should be noted that the ^{15}N concentration in product ammonia was always lower than that in nitrogen; i.e., 42.2%. The rest must be retained in the catalyst. The amount of nitrogen-15 (V_{15}) retained in the catalyst can be calculated from the following integration on the basis of the results shown in Fig. 6.

$$V_{15} = \int_0^{122} R_N (C_i - C_o)dt,$$

where R_N is the reaction rate of nitrogen and C_i and C_o are inlet and outlet concentration of ^{15}N respectively.† A value of 1.48×10^{-4} g-atm ^{15}N, i.e., 1.7 ml(STP) of ^{30}N$_2$, was found for V_{15}.

* According to a recent report by Moore and Unterwald (10), long induction periods were observed before appearance of ^{15}NH$_3$ in a similar experiment under very low pressure (~10^{-6} Torr).

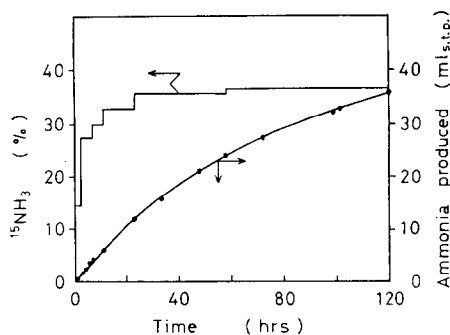† $C_i = 0.422$, C_o is given by the top curve in Fig. 6.

Hydrogenation of Nitride

H.K.R. concluded that the rate of ammonia synthesis was controlled by one of the steps in the conversion of adsorbed nitrogen to ammonia partly because the formation of ammonia continued with unchanged rate for a period after the removal of gas phase nitrogen. The same experiment was carried out except that the temperature was not changed on replacement of reactant gas. The procedure adopted was to interrupt the synthesis by evacuation for 1 min, to replace the N$_2$ + 3H$_2$ mixture by hydrogen of the same partial pressure as in the synthesis and to measure the rate of formation of ammonia. The time course of the amount of nitrogen hydrogenated is illustrated in Fig. 7. The
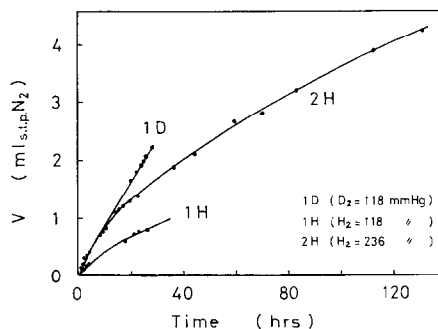

Fig. 7. Hydrogenation of nitride at 330°C after used for synthesis. V, the amount of nitrogen hydrogenated. Flow rate in 1D and 1H are equal (2.1 liters (STP)/hr). Hydrogen partial pressure in the previous synthesis for 1D, 1H, and 2H are 118, 118, and 69 mm Hg, respectively.
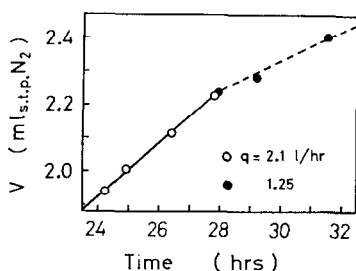
FIG. 8. The effect of flow rate (q) on the hydrogenation rate of nitride. V, the amount of nitrogen hydrogenated; P_{D2}, 118 mm Hg; Reaction temp., 330°C.

initial rate of hydrogenation (within 2 hr) are read to be 0.09 ml N_2/hr for hydrogen of 118 mm Hg and 0.17 ml N_2/hr for deuterium of 118 mm Hg. The corresponding rates of synthesis in the previous steady state were 0.13 and 0.22 ml N_2/hr, respectively. Since the very initial rate of hydrogenation after the replacement seems to be somewhat larger than the above value, the synthesis rate may be considered to agree with the initial rate of hydrogenation as stated by H.K.R.

Another characteristic feature of this hydrogenation process to be noted is that the reaction rate depends on the flow rate of hydrogen as observed for the synthesis. The effect of flow rate is shown in Fig. 8.

Another run of hydrogenation of sorbed nitrogen was made by 236 mm Hg of hydrogen with the ^{15}N enriched nitride which was obtained by the previously described synthesis with the enriched nitrogen and
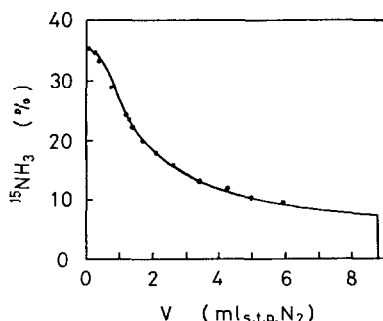

FIG. 9. [15]N concentration in ammonia formed from nitride as a function of the amount of nitrogen consumed. The nitride was previously used for ammonia synthesis with the ^{15}N-enriched nitrogen.

contained 1.7 ml(STP) of [30]N_2. The ^{15}N concentration in ammonia thus obtained is plotted in Fig. 9 as a function of the amount of nitrogen consumed. The total amount of ^{15}N eluted was 1.14×10^{-4} g-atm; i.e., 1.3 ml(STP) of [30]N_2 which amounts to 77% of the total ^{15}N absorbed. This suggests that ^{15}N in the catalyst was located near to the surface in the bulk.

DISCUSSION

Rate-Determining Step of Ammonia Synthesis

When the concept of rate-determining step is applied to the over-all rate, the discussion based on observations of an elementary step such as the nitridation or its hydrogenation must be careful for a possible deviation of surface state from the real one. For instance, the rate of nitridation seriously depends on the extent of nitridation. In this respect the conclusion derived by H.K.R. is to be reexamined.

Since nitrogen adsorption and the hydrogenation of adsorbed nitrogen are admittedly possible rate-determining step in ammonia synthesis (Eq. (6)), the present discussion will be confined to these two steps assuming other steps to be in equilibrium. If the two steps are represented by Eqs. (i) and (ii),

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (6)$$
$$N_2 \rightarrow 2N(a) \qquad (i)$$
$$N(a) + 3H(a) \rightarrow NH_3 \qquad (ii)$$
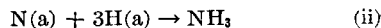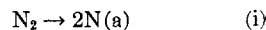
the steady rate of nitrogen consumption R_s should obey the relationship,

$$R_S = r_{+1} - r_{-1} = \tfrac{1}{2}(r_{+2} - r_{-2}), \qquad (7)$$

where r_{+1}, r_{-1}, r_{+2}, and r_{-2} indicate the forward and backward rate of the elementary step (i) and (ii), respectively. Equation (7) becomes (1)

$$R_S = r_{+1}(1 - r_{-1}/r_{+1})$$
$$= r_{+1}(1 - \exp(\Delta F_1/RT)), \quad (8)$$

where ΔF_1 is the free energy change due to the step (i). ΔF_2 for the step (ii) is given in terms of the free energy change ΔF due to the over-all reaction (Eq. (6)), as follows:

$$\Delta F = RT \ln \eta^2 \qquad (9)$$

$$\Delta F = \Delta F_1 + 2\Delta F_2, \qquad (10)$$

where $\eta = (NH_3)/(NH_3)_e$ is the efficiency of the reaction.

If the rate of reaction is determined by the step (ii) as supposed by H.K.R., the step (i) should be in equilibrium, namely,

$$\Delta F_1 \eqsim 0$$

$$r_{+1} \eqsim r_{-1}.$$

Hence, there should be observed an isotopic mixing in the reactant nitrogen during the synthesis run, whereas this was not shown by the present result, suggesting step (i) as the rate-determining step. The absence of isotopic mixing is quite reasonable when the rate of reaction is determined by step (i).

A possible extent of the isotopic mixing is estimated for the following two cases:

$$\Delta F_1 = \Delta F$$
$$r_{-1} = \eta^2 r_{+1} \eqsim \eta^2 R_S \qquad (a)$$
$$\Delta F_1 = \tfrac{1}{2}\Delta F$$
$$r_{-1} = \eta r_{+1} \eqsim \eta R_S. \qquad (b)$$

The rate of formation (1) of $^{29}N_2$ is given by

$$\frac{d}{dt}(nz) = 2x(1-x)r_{-1} - zr_{+1}, \qquad (11)$$

where n is the amount of nitrogen in the system (mole), z the mole fraction of $^{29}N_2$ and x the atomic fraction of ^{15}N in the adsorbed phase. Considering

$$-\frac{dn}{dt} = R_S = r_{+1} - r_{-1},$$

Eq. (11) is transformed to

$$\frac{dz}{dt} = \frac{r_{-1}}{n}(2x(1-x) - z). \qquad (12)$$

It is assumed that the value of x is equal to the ^{15}N fraction in ammonia. This might lead to underestimation of dz/dt for (b), but it is a safer estimation. Other variables in Eq. (12)—n, z, and r_{-1} ($=\eta^2 R_s$ or ηR_s)—are available as function of time, whereas z can be regarded to be constant at 26.6%. By a graphical integration of

Eq. (12) the expected increase in z during 122 hr is estimated as follows: Case a, 0.2%; case b, 1.6%. The increase expected for case b clearly exceeds the experimental error in this study. Hence, case b can be excluded also.

Kinetics and Isotope Effect

On the basis of the above discussion, three rate equations relevant to the step of nitrogen adsorption are examined. Since the contribution of backward reaction was proved to be negligible, the backward rate of reaction will be neglected in the following treatment. Three equations tested are as follows:

(a) Temkin equation

$$R = \frac{dy}{d(1/q)} = kP_{N2}(P_{H2}^3/P_{NH3}^2)^\alpha$$
$$= kP^{1+\alpha}y^{-2\alpha} \qquad (13)$$

(b) Langmuir-type equation with the main adsorbed species of NH

$$R = \frac{dy}{d(1/q)} = \frac{k'P_{N2}}{(1 + K'P_{NH3}/P_{H2})^2}$$
$$= \frac{kP}{(1 + Ky)^2} \qquad (14)$$

(c) Langmuir-type equation with the main adsorbed species of N

$$R = \frac{dy}{d(1/q)} = \frac{k'P_{N2}}{(1 + K'P_{NH3}/P_{H2}^{1.5})^2}$$
$$= \frac{kP}{(1 + Ky/\sqrt{P})^2}, \qquad (15)$$

where P (atm) is the total pressure ($4P_{N2}$), and k, K, and α are constants. The best constants for each equation which incorporate the experimental results at 330°C were selected by the integral form of these equations using electronic computer (FACOM 222) (5). The standard deviations (S) of k were calculated as follows:

$$S^2 = \frac{1}{n_H - 1}\sum^{n_H}\left(\frac{k_H - k_{av}}{k_{av}}\right)^2$$

for Eq. (13), and

$$S^2 = \frac{1}{n_H + n_D - 1}\left[\sum^{n_H}\left(\frac{k_H - k_{av}}{k_{av}}\right)^2 + \sum^{n_D}\left(\frac{k_D - k_{av}}{k_{av}}\right)^2\right]$$

for Eqs. (14) and (15), and are listed in Table 2. Since k is defined as the rate constant of nitrogen chemisorption, a same value of k was allotted to both hydrogen and deuterium system for Eqs. (14) and (15). The best equation may be selected by the value of S. Although the difference in S between Eqs. (14) and (15) is not so extensive, Eq. (15) is the best one. The relation between y and $1/q$ derived from Eq. (15) is reproduced as a solid line in Figs. 3 and 4 using the best constant in Table 2.

It may be concluded from the above analysis that the rate-determining chemisorption of nitrogen is retarded by the adsorbed atomic nitrogen which is equilibrated with ammonia and hydrogen in the gas phase. This situation is the same as concluded with the unpromoted iron (5). The isotope effect is caused by the difference in the adsorption constant K in Eq. (15). As was previously reported, the ratio K_H/K_D is equal to the ratio of the equilibrium constant of ammonia decomposition. The latter ratio is calculated to be 3.82, while the former ratio obtained from Table 2 is 3.2. Considering that the D concentration in the reactant deuterium was 95%, the experimental value becomes closer to the theoretical one.

As shown in Fig. 5, the heat effect on the rate of synthesis was a little higher in the D system, with a difference of 0.8 kcal/mole. In other words, the isotope effect was more extensive at higher temperature. This result is anomalous for the isotope effect of kinetic origin, but quite reasonable for the case as described by the Eq. (15). That is, according to Eq. (15), the inverse effect is due to the relative magnitude of $Ky/(P)^{1/2}$ to unity in the denominater. The concentration of ammonia (y) seems to be so low at lower temperature that the term $Ky/(P)^{1/2}$ is negligible to unity, equalizing both rates. Such situation is realized when the temperature coefficient of K is less extensive than that of y. The latter may be approximated to the apparent activation energy obtainable from Fig. 5; i.e., about 13 kcal/mole. The evaluation of the former needs more data at different

temperatures, but the value seems to be small as observed previously over the promoted iron (4). This is reasonable when it is recalled that K is the equilibrium constant of the reaction

$$NH_3 = N(a) + \tfrac{3}{2}H_2$$
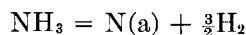
because the heat effect in K is less than the heat of dissociative adsorption of nitrogen by an amount corresponding to the heat of ammonia synthesis.

TABLE 2

The Best Constants and Standard Deviations for Eqs. (13), (14), and (15). (330°C)

Eq.	System	α or K	k	S (%)
(13)	H	$\alpha = 0.50$	0.00127	44.5
	D	$\alpha = 0.61$	0.0915	36.9
(14)	H	$K = 1830$	0.0019	17.6
	D	$K = 400$		
(15)	H	$K = 1900$	0.0025	12.4
	D	$K = 600$		

The Exchange between Adsorbed Nitrogen and Bulk Nitride

As illustrated in Fig. 6, the result of the synthesis by ^{15}N-enriched nitrogen shows that the ^{15}N concentration in ammonia increases rapidly in the initial period and then gradually in the later period, but it is unlikely to attain the original value of 42.2%. This indicates that ^{15}N was partly lost into an unreactive form of nitrogen, probably the bulk nitrogen.

The initial rapid increase of ^{15}N in ammonia seems to result from the isotopic mixing in the adsorbed nitrogen. Since the reactant nitrogen containing fixed concentration of ^{15}N is continuously supplied to the adsorbed phase, the ^{15}N in ammonia should attain, after completion of the mixing, the same concentration as in the reactant nitrogen, provided that no exchange takes place between the adsorbed and bulk nitrogens. Hence, the result shown in Fig. 6 provides an evidence for the exchange. The later slow increase of ^{15}N in ammonia seems to reflect a gradual increase of [15]N

in the bulk. This is reasonable considering the larger amount of nitrogen in the bulk.

On the basis of above discussion, it may be permissible to assume that a quasi steady value of ^{15}N concentration in the adsorbed phase was attained in the later stage. This value can be assessed as about 35.5% from Fig. 6. The ^{15}N concentration in the bulk seems to be negligibly small at this stage. Hence the ^{15}N atoms coming into the adsorbed phase via the chemisorption process should be divided to two directions, i.e., to ammonia and to the bulk. This can be represented by the equation

$$0.422R = 0.355R + 0.355E, \quad (16)$$

where R is the steady rate of ammonia synthesis in N atoms/time and E the rate of exchange between the adsorbed phase and the bulk. This relation gives the relative rate $R/E = 5$.

A similar balance in ^{15}N can be applied for the initial stage of displacement and is represented, assuming uniformity of adsorbed nitrogen, by the equation

$$V_N \frac{dx}{dt} = 0.422R - x(R + E), \quad (17)$$

where V_N is the amount of adsorbed nitrogen and x the ^{15}N concentration in the adsorbed phase. Equation (17) is integrated to

$$\ln \frac{0.355 - x}{0.355} = -\frac{1.19R}{V_N} t. \quad (18)$$

If x can be approximated to ^{15}N concentration in ammonia as assumed for the later stage, Eq. (18) can be plotted as shown in Fig. 10. The plots are not on a straight line as expected by Eq. (18). This result suggests the heterogeneity of the adsorbed nitrogen. The amount of adsorbed nitrogen which is most active and thus responsible for the steady rate may be estimated from the initial slope of the curve. This amounts to 1.0 ml(STP)N_2.

Hydrogenation of Nitride

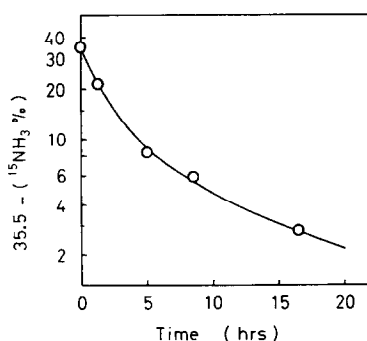It was found that the initial rate of hydrogenation of nitride was nearly equal

FIG. 10. Plot of Eq. (18).

to the previous rate of synthesis in the steady state. On the basis of such finding, H.K.R. concluded that the hydrogenation process was the rate-determining step. This is contradictory to the conclusion of present study where the process of hydrogenation is considered to be equilibrated as assumed for the rate equation (15) and for Eq. (17).

According to the present view, the process of hydrogenation should be equilibrated also in the case of hydrogenation of nitride. If this was the case, the observed rate of formation is represented by the equation

$$\text{Rate} = fq KNP_{H_2}^{1.5}, \quad (19)$$

where q is the flow rate, N the effective amount of adsorbed nitrogen, P_{H_2} the partial pressure of hydrogen, f a constant, and K is the equilibrium constant of the reaction

$$N(a) + 1.5H_2 = NH_3.$$
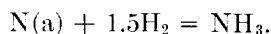
The dependency of the rate on P_{H_2} was proved already by H.K.R. The inverse isotope effect on the rate of hydrogenation as shown in Fig. 7 is reasonable on the ground of Eq. (19) because K_D is 3.8 times as large as K_H, whereas this is improbable by the H.K.R. mechanism.

The linear dependency on the flow rate is suggested by the result shown in Fig. 8. The rate of hydrogenation was decreased from 1.60 to 0.92 ml(STP)N_2/hr by the decrease in the flow rate from 2.1 to 1.25 liter(STP)/hr. The ratio 0.58 for the re-

action rate agrees with 0.60 for the flow rate.

Thus, the rate of hydrogenation exhibits the kinetic features as expected by Eq. (19). Accordingly, the initial rate of hydrogenation should depend on the value of N in Eq. (19). Since the ammonia concentration in the effluent gas from the catalyst bed is extremely small, variation of the amount of adsorbed nitrogen with time is expected to be less significant. This is the reason why the rate of hydrogenation remains at the same rate as the previous rate of synthesis after the removal of nitrogen from the system.

As reported by H.K.R. (500°C) and shown in Fig. 7 (330°C), the fast initial process in the hydrogenation of nitride was followed by a slower process which continued at a steady rate for hours, with the latter process starting earlier at a higher temperature. The steady rate in the later stage was claimed by H.K.R. to be due to a constant concentration of the adsorbed nitrogen which is expected to be determined thermodynamically by the bulk nitride.

According to Eq. (19) the decrease in the rate of hydrogenation should be ascribed to the decrease in the effective amount of adsorbed nitrogen N. This is natural simply because the hydrogenation consumes the adsorbed nitrogen. Thus, the steady rate in the later stage may be due to steady amount of the adsorbed nitrogen. If this were the case, the deuterium isotope effect on the steady rate should be given by the ratio K_D/K_H; i.e., 3.8 at 330°C. The observed relative rate in the later stage is obtained from Fig. 7 to be $7.5/2.1 = 3.6$, which is in a satisfactory agreement with the expected value. Thus, the result of the present study supports the view adopted by H.K.R., as far as the steady rate of hydrogenation of nitride in the later stage is concerned.

The steadyness of the amount of adsorbed nitrogen concluded above should be examined also on the ground of relative rate. The relative value of the steady rate of synthesis (R) to the rate of exchange (r) between the adsorbed and the bulk nitrogen is estimated to be about 5 as

previously described. In the case of the steady state of hydrogenation, the rate of nitrogen consumption was about 5 times as low as the initial rate which was nearly equal to the steady rate of synthesis. Since the decrease in the rate of nitrogen consumption is due to shortage of the adsorbed nitrogen, the rate of nitrogen supply from the bulk would be larger than r which was obtained in the steady state of synthesis run. Thus, the steadiness in the amount of adsorbed nitrogen would be reasonable in this condition.

When the above conclusion is applied to the time course of ^{15}N elution from the ^{15}N-containing catalyst as shown in Fig. 9, the convex curve in the initial stage is quite reasonable since the adsorbed nitrogen of higher ^{15}N concentration is to be hydrogenated first.

It should be concluded from above discussions that the mechanism of ammonia synthesis on molybdenum nitride is similar to that previously reported for iron nitride by Logan, Moss, and Kemball (*11*), and is shown as follows:

$$N_2 \rightarrow N(a) \rightleftharpoons NH_3.$$
$$\Updownarrow$$
$$Mo_2N$$
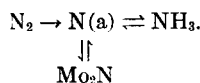
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