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Isotopic Mixing in Nitrogen Over a Doubly Promoted Iron*

YUTAKA MORIKAWA AND ATSUMU OZAKI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
Ohokayama, Meguroku, Tokyo, Japan

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The rate of displacement of adsorbed nitrogen under the adsorption equilibrium over a doubly promoted iron catalyst was determined at 250 and 350°C by means of isotopic nitrogen, and compared with the rate of isotopic exchange of nitrogen molecule. Although the rate of displacement is not uniform with respect to the adsorbed nitrogen, the highest rate of displacement is in agreement with the rate of isotopic mixing. It is accordingly concluded that the adsorbed nitrogen is mostly dissociated. A remarkable acceleration of the isotopic exchange is observed in the presence of hydrogen, and a normal isotope effect of 1.07 is determined for the acceleration by hydrogen. It is accordingly concluded that the acceleration effect is chemical in nature and that the promoter K_2O is responsible for the acceleration by hydrogen as well as for the increase in the rate of isotopic exchange in the absence of hydrogen.

INTRODUCTION

In the preceding paper (*1*), it has been shown that a large part of adsorbed nitrogen over unpromoted iron is undissociated. This conclusion was derived from the rate of displacement of preadsorbed nitrogen under an adsorption equilibrium which was faster than the rate of isotopic mixing reaction,

$$^{28}N_2 + {}^{30}N_2 \rightleftharpoons 2\,{}^{29}N_2. \quad (1)$$

It has been also shown (*1*) that the added hydrogen over the unpromoted iron has no accelerating effect upon the isotopic mixing, contrary to the results by Joris and Taylor (*2*) and Kummer and Emmett (*3*) over promoted iron catalysts.

In the previous paper (*4*), it has been shown that the main adsorbed species during the ammonia synthesis is nitrogen atom over the unpromoted iron, in marked contrast to imino radical reported over doubly promoted iron catalyst (*5*).

It is obvious that the unpromoted iron and the doubly promoted iron behave differently to hydrogen in the ammonia synthesis and in the isotopic mixing in nitrogen. However Logan and Philp (*6*) reanalyzed† the data of Ozaki *et al.* (*5*) (OTB) and suggested that the main adsorbed species over the doubly promoted iron could be the nitrogen atom instead of the imino radical previously proposed if the chemisorption of nitrogen is promoted by hydrogen twice as fast as by deuterium. This may be tested by the deuterium isotope effect of the promotion of isotopic mixing in nitrogen over the doubly promoted iron.

In addition to this prediction, application of the displacement method of adsorbed state study to the adsorbed nitrogen over the doubly promoted iron seems important in connection with the mechanism of ammonia synthesis.

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* Most part of this work was presented at the 25th discussion of the Catal. Soc. Japan (Oct. 1969).

† There were mistakes in quoting data from OTB paper.

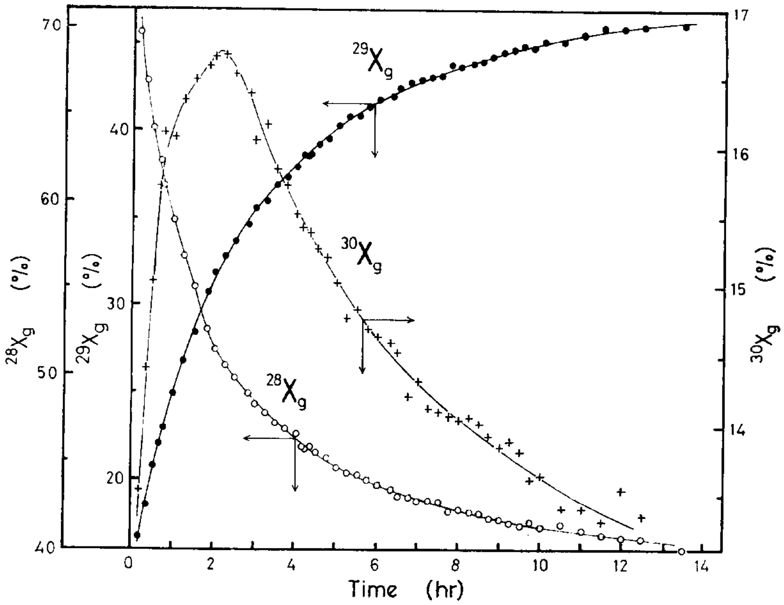

FIG. 1. Time course of the mole fraction of $^{28}N_2$, $^{29}N_2$, and $^{30}N_2$ ($^{28}X_g$, $^{29}X_g$, and $^{30}X_g$), resulted from the displacement at 350°C.

EXPERIMENTAL METHODS

The doubly promoted iron catalyst[1] was obtained from the Government Chemical Industrial Research Institute. The catalyst grain was crushed to 8 to 10 mesh. The amount of catalyst used was 21.2 g before reduction. The catalyst was reduced in the reaction vessel by circulating hydrogen at 400°C for 40 days and at 500°C for 20 days. The catalyst after reduction had a total surface area of 297 m² and contained 4.9% Al_2O_3; 1.0% CaO; and 0.7% K_2O by wt. All gases used here were deoxygenized by passing through a reduced copper-kieselguhr column at 200°C. Heavy nitrogen of 70.0% ^{15}N was prepared by the same method as in the previous paper.

The procedure to follow the displacement process of adsorbed nitrogen was described in the previous paper (*1*), that is, the time course of isotopic composition of gaseous nitrogen was followed in a circulating system after mixing light and heavy nitrogen of equal pressure which were separately placed in the apparatus before mixing. The heavy nitrogen part was adsorbed and equilibrated with the catalyst in advance. The isotopic composition was continuously followed by quadrupole mass spectrometry. The gas sample was taken out through a sampling leak attached to the circulating system. But the leak was so small that the amount of gas sample taken out was negligible. In cases where the runs took a long time, a few gas samples were intermittently taken out instead of the continuous sampling. Before each run, the catalyst was treated with hydrogen at 400°C for 24 hr to remove adsorbed nitrogen and then evacuated at 400°C for 20 hr. No gas desorption from the catalyst was detected at the reaction temperature by the quadrupole mass spectrometer after this treatment.

RESULT

The changes in the mole fractions $^{28}X_g$, $^{29}X_g$, and $^{30}X_g$ of $^{28}N_2$, $^{29}N_2$, and $^{30}N_2$ observed in the displacement of adsorbed heavy nitrogen (0.45 mmole on 21 g or 1.5×10^{-3} mmole/m²) at 350°C under

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[1] This catalyst is actually triply promoted. But the term "doubly" is used to mean a catalyst containing both K_2O and Al_2O_3.

378 mm Hg are shown in Fig. 1. The value of ${}^iX_g$ is intermittently calculated from the continuous analysis data. The time course of ${}^{30}X_g$ clearly reflects the experimental condition in which the initial isotopic concentration is higher in the adsorbed phase than in the gas phase. The ${}^{30}X_g$ initially increases with time because of the desorption of ${}^{30}N_2$ molecules from the adsorbed phase, while ${}^{30}N_2$ is concurrently consumed by the isotopic mixing reaction. Thus ${}^{30}X_g$ reaches maximum after a while of increase, whereas ${}^{29}X_g$ monotonously increases with time because both the desorption of ${}^{29}N_2$ and the isotopic mixing give rise to increase in ${}^{29}X_g$. On the other hand, the atomic fraction of ${}^{15}N$ in the gas phase (f_g) solely depends on the displacement process. Thus the time course of the displacement process can be followed by f_g.

Displacement

The intermittent values of f_g are calculated from ${}^{29}X_g$ and ${}^{30}X_g$ of Fig. 1, and plotted against time in Fig. 2, where f_{g0} is the value of f_g at time zero and $f_{g\infty}$ is the value of f_g expected on the complete displacement. Figure 2 shows that the displacement results in an increase in f_g up to a plateau value in about 9 hr and that the plateau value is in agreement with $f_{g\infty}$. From this fact it is concluded that all the adsorbed nitrogen is displaceable at 350°C.

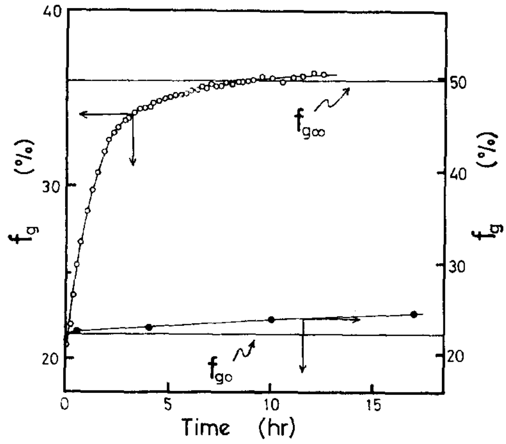

FIG. 2. Time course of the atomic fraction of ${}^{15}N$ (f_g) resulted from the displacement at 350°C (○); and 250°C (●).

Another run of the displacement was carried out at 250°C under 94.5 mm Hg. At this temperature the adsorption was so slow that more than 2 days were taken to establish the adsorption equilibrium. The time course of f_g at 250°C is shown in Fig. 2. The displacement is very slow from the initial stage reaching only 10% of adsorbed nitrogen in initial 17 hr.

The rate of displacement, V, can be expressed (*1*) by:

$$Vt = \frac{-2.3 n_g n_s}{n_g + n_s} \log \frac{(f_{g\infty} - f_g)}{(f_{g\infty} - f_{g0})}, \qquad (2)$$

where n_g and n_s are, respectively, the number of nitrogen molecules in the gas phase and the adsorbed phase. It is suggested by this relation that if the rate of displacement, V, is uniform among the adsorbed nitrogen, a plot of $\log(f_{g\infty} - f_g)$ against t should be linear and the value of V can be calculated from the slope of the linear plot. However, as shown in Fig. 3a and b, the plot is undoubtedly curved. The curved plot shows that the preadsorbed nitrogen is displaced faster in earlier stage than in later period. The initial value of V is estimated from the slope at time zero to be 11.3×10^{15} (molecules/min·m^2) at 350°C and 4.2×10^{13} (molecules/min·m^2) at 250°C.

Isotopic Mixing

If the isotopic concentration in the gas phase is equal to that in the adsorbed phase, the rate of isotopic mixing, R, is expressed by

$$Rt = -2.3 n_g \log \frac{|{}^iX_{g\infty} - {}^iX_g|}{|{}^iX_{g\infty} - {}^iX_{g0}|}, \qquad (3)$$

where ${}^iX_g$, ${}^iX_{g0}$, and ${}^iX_{g\infty}$ are, respectively, the mole fractions of ${}^iN_2$ at time t, zero, and the equilibrium. R also gives the rate of dissociative adsorption of nitrogen which is equalized to the rate of desorption of the dissociated nitrogen under the reaction condition. $|{}^iX_{g\infty} - {}^iX_g|$ of the run at 350°C is plotted against t for the later period where f_g is nearly equal to $f_{g\infty}$ as shown in Fig. 2. The plot is shown in

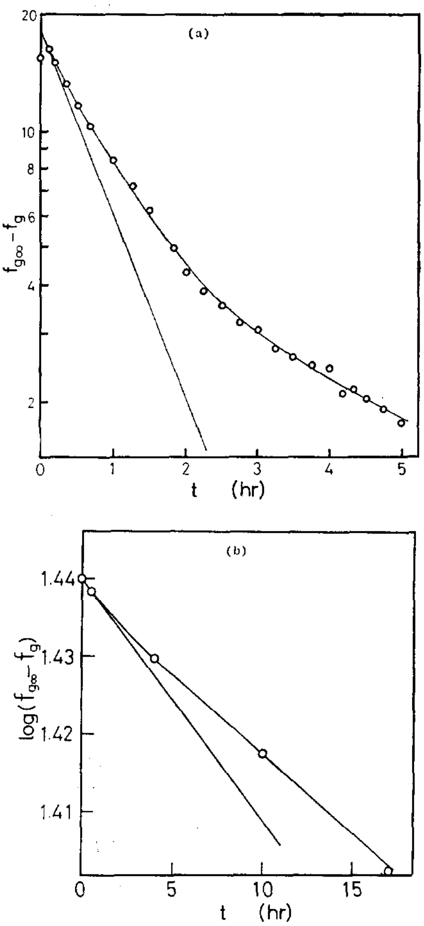

FIG. 3a. Log plot of $f_{g\infty} - f_g$ vs t in connection with Eq. (2), based on the data in Fig. 2 (at 350°C). The straight line shows the slope at time zero. (b) Plot of $\log(f_{g\infty} - f_g)$ vs t in connection with Eq. (2), based on the data in Fig. 2 (at 250°C). The straight line shows the slope at time zero.

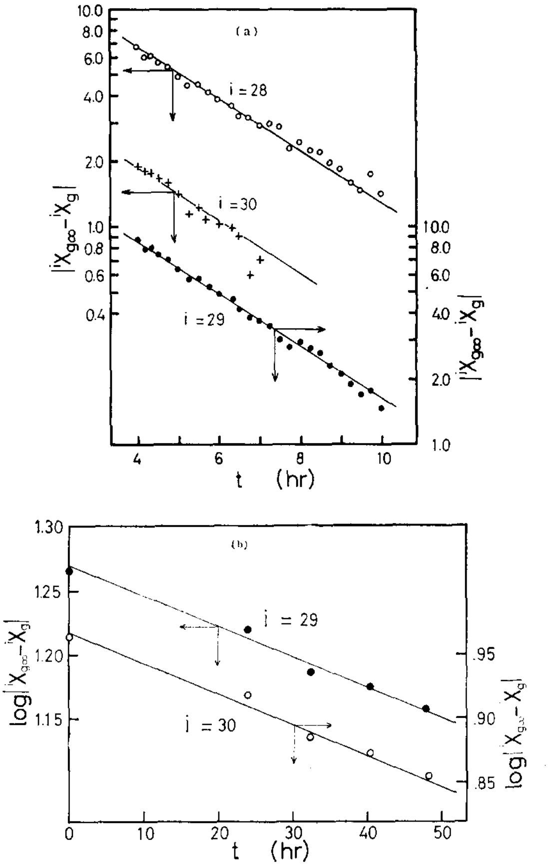

FIG. 4a. Log plot of $|{}^iX_{g\infty} - {}^iX_g|$ vs t in connection with Eq. (3), based on the data in Fig. 1. (b) Plot of $\log|{}^iX_{g\infty} - {}^iX_g|$ vs t in connection with Eq. (3), resulted from the isotopic mixing at 250°C.

Fig. 4a, where the absolute value of $|{}^iX_{g\infty} - {}^iX_g|$ is plotted on the ordinate. Those plots of ${}^{28}X_g$, ${}^{29}X_g$, and ${}^{30}X_g$ are linear as expected and are parallel each other, demonstrating validity of Eq. (3). Thus the value of R can be determined from the slope of the straight line and the calculation gives a value of 10.6×10^{15} (molecules/min·m^2) which is in agreement with the initial value of V. Since the rate of displacement at 250°C was so slow that the condition of $f_g \fallingdotseq f_{g\infty}$ required for the plot of Eq. (3) was not realized in the course of the displacement run. Thus a separate run for the isotopic mixing was carried out at 250°C, where the reaction mixture instead of the isotopic nitrogen was preadsorbed. The result is shown as a plot of Eq. (3) in Fig. 4b from which R at 250°C is calculated to be 4.31×10^{13} (molecules/min·m^2).

Effect of Hydrogen on the Isotopic Mixing

A small amount of hydrogen was introduced into the reaction system of the isotopic mixing at 350°C under a condition of $f_s = f_g$, where f_s is the atomic fraction of ^{15}N in the adsorbed phase. The resulting plots of $|{}^iX_{g\infty} - {}^iX_g|$ vs t are shown in Fig. 5a, where the arrow shows the time when hydrogen was introduced. It is clear that the rate of mixing abruptly increases

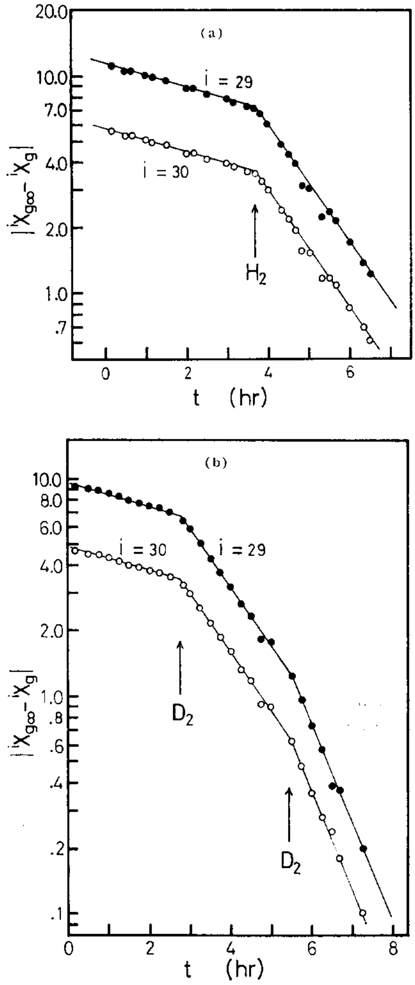

FIG. 5a. Log plot of $|^iX_{g\infty} - {}^iX_g|$ vs t in connection with Eq. (3); (arrow) time when hydrogen was introduced into the reaction system. (b) Log plot of $|^iX_{g\infty} - {}^iX_g|$ vs t in connection with Eq. (3); (arrows) time when deuterium was introduced into the reaction system twice.

on introduction of hydrogen. The extent of increase is about five times. This result clearly demonstrates that the isotopic mixing of nitrogen over the doubly promoted iron catalyst is remarkably accelerated by the presence of hydrogen in agreement with the previous paper (*2*). Since only a trace amount of hydrogen was detected in the gas phase by mass spectrometric analysis 1 hr after introduction of hydrogen, the most part of the added hydrogen seemed to be adsorbed by the catalyst. The nitrogen pressure was slightly decreased by introduction of hydrogen, giving a 3% increase in the amount of adsorbed nitrogen in 2.5 hr after introduction of hydrogen. The increase in the rate of isotopic mixing on introduction of hydrogen cannot be due to this slight increase in the amount of adsorbed nitrogen.

Under the same condition, the accelerating effect of deuterium, instead of hydrogen, was examined. The resulting plots are shown in Fig. 5b, where the effect of amount of the added deuterium is also shown.

The rates of isotopic mixing, R, are obtained from slopes of these plots and are tabulated in Table 1, where the rate data obtained at 325 and 370°C are also shown. The value of R is lower than that obtained from Fig. 4a because there was an accidental introduction of air over the catalyst after the run shown in Fig. 4a. The subsequent hydrogen treatment at 450°C failed to reproduce the original activity.

The extent of acceleration, η, is defined for convenience as ratio of the accelerated rate (R_H) over the original one (R). In this way the possible variations in R are cancelled. Table 1 shows clearly that η increases with the amount of deuterium added. Although the amount of hydrogen or deuterium added was fixed at around 0.14 mmole in the other runs, the slight differences in the added amount are corrected by interpolation on the basis of the observed effect of amount of added deuterium. The corrected value of η is denoted as η' and shown in the last column of Table 1. A slight but definite deuterium isotope effect in the acceleration is observed. The ratio of mean values of η'_H and η'_D is 1.07. The heat effect on the rate of mixing is estimated to be 30.0 kcal/mole for R and 28 kcal/mole for R_H.

DISCUSSION

1. The Adsorbed Species of Nitrogen Over the Doubly Promoted Iron

The plot corresponding to Eq. (2), as shown in Fig. 3a and b, reveals that the rate of displacement decreases with the ex-

TABLE 1
THE EFFECT OF HYDROGEN ON THE RATES OF ISOTOPIC MIXING

Run	Temp (°C)	n_g (mmole)	Added hydrogen (mmole)	$R \times 10^{-15}$ (molecules/ $m^2 \cdot min$)	$R_H \times 10^{-15}$ (molecules/ $m^2 \cdot min$)	$\eta = R_H/R$	η' (0.1400 mmole)	
1	350	1.040	H_2 0.1326	4.23	22.6	5.34	5.60	η'_H
2		1.047	H_2 0.1387	4.36	22.6	5.18	5.23	
3		1.060	D_2 0.1376	4.44	22.3	5.02	5.10	η'_D
		1.060	D_2 0.2664	4.44	36.7	8.27		
4		1.062	D_2 0.1436	4.87	25.0	5.13	5.01	
5	370	1.039	H_2 0.1449	9.38	42.8	4.57		
6	325	1.059	H_2 0.1374	1.58	7.02	4.44		

tent of displacement. It seems that there exists a distribution of desorption rates among the adsorbed nitrogen. The initial rate of displacement, V, is the highest one so that it should be identical with the overall rate of desorption equalized with that of adsorption at the adsorption equilibrium. The rate of displacement in the later stage represents the rate of desorption of more tightly bound nitrogen. The overall rate of desorption at the adsorption equilibrium thus obtained by V is in agreement with the rate of desorption of dissociated nitrogen obtained by R both at 350 and 250°C. The result clearly demonstrates that the displacement takes place mostly by way of the dissociative adsorption. If there are a detectable amount of undissociated adsorbed nitrogen molecules, they should be displaced faster than the dissociated nitrogen. Accordingly most of the adsorbed nitrogen seems dissociated in the temperature range 250 to 350°C.

The displacement of the adsorbed nitrogen over the unpromoted iron was found to take place faster than the isotopic mixing. Thus it was concluded in the previous paper (*1*) that the adsorbed nitrogen is largely undissociated over the unpromoted iron, with some dissociated nitrogen causing the isotopic mixing. That is,

$$N_2(g) \rightleftharpoons N_2(a) \rightleftharpoons 2N(a). \qquad (4)$$

It is difficult, however, to detect $N_2(a)$ over the promoted iron catalyst.

The amounts of adsorbed nitrogen over the unpromoted and the promoted irons at 350°C and about 350 mmHg are as follows:

Unpromoted	3.5×10^{18} molecules/m^2 Fe
Promoted	0.9×10^{18} molecules/m^2 total area

If the area of exposed iron is 40% of total area as determined by Brunauer and Emmett (*7*), 2.3×10^{18} molecules/m^2 Fe is obtained for the promoted catalyst. These values show that the surface concentration of adsorbed nitrogen is not so different over both catalysts. Thus the observed difference in the feature of displacement indicates a transformation of adsorbed state.

This difference in the adsorbed nitrogen between the unpromoted and the promoted irons seems interesting and important. The role of alumina as the promoter is admittedly to provide a high surface area of iron against sintering (*8*). The difference in the adsorbed species accordingly seems to be caused by the other promoters, K_2O and CaO. These promoters are known to lower the work function of iron catalyst (*9*). The difference seems understandable on this basis as follows: Since there is a considerable difference in electronegativity between nitrogen and iron, the adsorbed nitrogen atom tends to draw electron from iron. However, the number of electrons available for the adsorbed nitrogen is limited so that the unpromoted iron may not be able to provide enough electrons, thus favoring the undissociated adsorption of nitrogen. The electropositive promoters may change this situation resulting in stabilization of the dissociated nitrogen on the iron surface.

2. Acceleration of Isotopic Mixing by Hydrogen

The accelerating effect of hydrogen on the isotopic mixing of nitrogen over the doubly promoted iron was found by Joris and Taylor (*2*) 30 years ago but no definite mechanism has been elucidated. Tamaru (*10*) has suggested a cooperative chemisorption of nitrogen assisted by an electron donation from the coexistent hydrogen. If this effect of hydrogen works in the isotopic mixing, the deuterium isotope effect on η cannot be expected, because there is no difference between hydrogen and deuterium in their electron-donating strength. The observed isotope effect is not large but enough to rule out the electron-donating effect of hydrogen and to conclude that hydrogen is chemically involved in the dissociation of nitrogen molecule. It seems that the dissociation of nitrogen molecule is actually made in a way,

$$N_2 + 2H = 2NH, \qquad (5)$$

in the presence of hydrogen over the promoted iron.

As mentioned in the Introduction, Logan and Philp (*6*) have claimed the deuterium isotope effect in the hydrogen-accelerated dissociative adsorption of nitrogen to be 1.99 at 302°, 2.40 at 278° and 2.77 at 251° as values of k_H/k_D. Although such a large heat effect on k_H/k_D, which corresponds to 4 kcal/mole, is inconsistent in itself as admitted by the authors, even this large heat effect gives an estimate of 1.53 at 350° at which a normal isotope effect of 1.07 is determined in the present study. This result invalidate the assumptions made by Logan and Philp (*6*) in their reanalysis of the data of OTB on the isotope effect in ammonia synthesis, e.g., $\alpha = 0.8$ instead of $\alpha = 1.0$ in OTB paper (*5*). In other words the extent of deuterium isotope effect in the dissociative adsorption of nitrogen is too small to fit their view that the main species on the surface is the adsorbed N atom. Thus the present results reconfirm the previous conclusion of NH as the main species over the doubly promoted iron.

In the previous work by OTB, the rate constant of ammonia synthesis was the same for H_2 and D_2. Since the rate-determining step of the ammonia synthesis is the adsorption of nitrogen, a small extent of the isotope effect might exist in the rate constant on the basis of the present result. But the original conclusion of NH which is based upon the observed isotope effect on the adsorption coefficient of NH is completely unaffected by such a small extent of change in the rate constant as 7% which causes a less than 4% change in the adsorption coefficient.

It should be emphasized here that there is a striking correspondence between the effect of hydrogen on the isotopic mixing in nitrogen and the adsorbed species during ammonia synthesis as follows:

	Unpromoted	Doubly promoted
Acceleration of isotopic mixing by H_2	None	Extensive
Main species during NH_3 synthesis	N	NH

The difference between the unpromoted and the promoted catalysts must be again due to the electropositive promoter.

The rates of isotopic mixing at 350°C over the unpromoted and the promoted catalysts are shown in Table 2, where it is shown that the rate of isotopic mixing

TABLE 2
THE RATES OF ISOTOPIC MIXING AT 350°C

Catalyst	Unpromoted iron (*11*)	Doubly promoted iron[a]		
Amount of hydrogen added, 10^{18} molecules/m² Fe	None	None	0.7	1.3
Rate of mixing, 10^{15} molecules/min·m² Fe	3.0	11	56	92

[a] The exposed iron area is assumed to be 40% of the total area.

is increased by about 3 to 4 times in the promoted catalyst in the absence of hydrogen, and more than 30 times in the presence of hydrogen. Thus it seems that the acceleration by hydrogen takes an important part of the rate of isotopic mixing over the promoted catalyst. In other words, the acceleration by hydrogen is the essential effect of the catalyst promoter. If the isotopic mixing takes place via Eq. (5), and if the activation energy of this process is lower as apparently observed in this study, the essential nature of the acceleration by hydrogen is quite reasonable.

It was mentioned in the previous paper by Aika and Ozaki (*4*) that the addition of potash to iron reduces the extent of dissociation of ethane or ammonia on the surface, and this effect of potash was interpreted in terms of electron-donating nature of potash. That is, the increase in the electron concentration in iron caused by potash results in the reduction of bonding ability of the metal, thus transforming $\equiv$N to $=$NH. The findings in the present study may be understood on this basis.

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11. We found mistakes in numerical values of the rate of displacement (*V*) and exchange (*R*) reported in the previous paper (*1*). They should be corrected as follows;

	Wrong	Correct	
V (later)	$1.0\cdot10^{19}$	$1.1\cdot10^{18}$	(molecules/min)
(initial)	$5.0\cdot10^{19}$	$6.5\cdot10^{18}$	(molecules/min)
R (380°C)	$8.8\cdot10^{18}$	$0.94\cdot10^{18}$	(molecules/min)
(400°C)	$25.6\cdot10^{18}$	$2.8\cdot10^{18}$	(molecules/min)

Since the argument therein is based on the relative magnitude of *V* and *R*, these mistakes do not affect the conclusion made in the previous paper. The data shown in figures of the previous paper are consistent with the above corrected values.