Displacement of Adsorbed Nitrogen Accompanied by Isotopic Mixing over Unpromoted Iron

YUTAKA MORIKAWA AND ATSUMU OZAKI

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

The displacement process of adsorbed nitrogen was isotopically traced by measuring the time course of isotopic concentration in the gas phase after an abrupt change, holding the equilibrium condition for the adsorption. The isotopic mixing in nitrogen was also observed. The rate of displacement was much larger than that of the mixing. This finding provides evidence that a portion of adsorbed nitrogen desorbs without mixing. There must be some undissociated nitrogen adsorbed, the amount of which seems to reach more than 80% of the adsorbed nitrogen.

INTRODUCTION

The adsorption of nitrogen is an important step in ammonia synthesis. Many works have been reported on the adsorption of nitrogen on iron catalysts, some of which were directed to the problem of the adsorbed state. The heterogeneity in the adsorption of nitrogen over a doubly promoted catalyst was shown by Scholten et al. (1) in terms of heat of adsorption. An undissociated state of adsorbed nitrogen, in addition to the dissociated one, was mentioned by Scholten et al. on the basis of the entropy change due to the adsorption, and by Takezawa and Emmett (2) on the basis of the reactivity of the adsorbed nitrogen.

Such a heterogeneity of the adsorbed state may be detected by examining the time course of displacement of the adsorbed nitrogen, regardless of the reason for the heterogeneity. If the adsorbed state is heterogeneous, there must be differences in the rate of the displacement and the isotopic mixing. This prediction constitutes the basis of the present work.

The isotopic mixing in nitrogen molecules was first studied by Joris and Taylor (3) and later by Kummer and Emmett (4) and by McGeer and Taylor (5). However no kinetic measurement on the mixing has ever been done yet on any type of catalyst.

EXPERIMENTAL

Material. The iron catalyst was prepared by reduction of ferric oxide, which was obtained by precipitation from ferric nitrate using aqueous ammonia, followed by decomposing the shaped and dried precipitate at 500°C. The oxide of 22.0 g was reduced by circulating hydrogen at 400°C for 20 days in the reaction vessel. After this reduction no more formation of water was detected. The catalyst had a surface area of 1.6 m²/g.

Heavy nitrogen was prepared by adding an aqueous $(^{15}NH_4)_2SO_4$ solution to a paste of calcium hydroxide, followed by oxidizing the liberated $^{15}NH_3$ with hot cupric oxide to form free nitrogen. Obtained nitrogen contained 14.4% ^{15}N.

All gases to be used here were deoxygenized by passing through a copper-kieselguhr column, at 200°C.

Procedure. The apparatus is a circulating system which can be divided into two parts. Firstly, the enriched nitrogen was introduced to the part which involves the reactor and was adsorbed on the catalyst until an equilibrium was established at the reaction temperature. The ordinary nitrogen was introduced to the other part of the circulating system to the amount of a pressure exactly equal to the equilibrium pressure of the enriched nitrogen. Secondly, these two
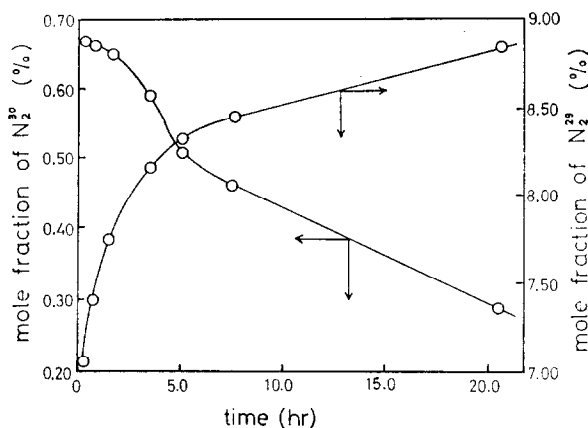
FIG. 1. Time course of the mole fraction of $^{29}N_2$ and $^{30}N_2$.

parts of gases were connected and circulated through the reactor. The mixing of the two gases was accomplished in a few minutes. This mixing could not affect the adsorption equilibrium in addition to the isotopic displacement because the pressures of the gases were equalized in advance.

The change in the isotopic composition of the circulating gas with time was measured by intermittent sampling. All analyses of gases were made by mass spectrometry.

RESULTS

The observed change in the isotopic composition of the gaseous nitrogen may be caused by two different processes. One is the intermolecular exchange of the nitrogen atoms, i.e., the isotopic mixing reaction

$$^{30}N_2 + {}^{28}N_2 = 2^{29}N_2 \tag{1}$$

which is observed as an increase in $^{29}N_2$ fraction and decreases both in $^{30}N_2$ and $^{28}N_2$. The other is the displacement of the adsorbed species by the gaseous nitrogen, which is caused by the difference in the isotopic concentrations between the gas and the adsorbed phases. The displacement process is observed as the increases both in $^{29}N_2$ and $^{30}N_2$ fractions in gas phase.

The mass spectrometric analysis of the gaseous nitrogen provides two kinds of information, i.e., the increase in the atomic fraction of ^{15}N and the decreases in the mole fractions of $^{28}N_2$ and $^{30}N_2$ with time. The former is caused solely by the displace-

ment process, while the latter is caused by both the isotopic mixing reaction and the displacement process.

The time courses of the changes in the mole fractions of $^{29}N_2$ and $^{30}N_2$ are shown in Fig. 1; they were obtained from the run at 380°C under 357 mm Hg. It is obvious from Fig. 1, that the isotopic mixing took place, because $^{29}N_2$ increases while $^{30}N_2$ decreases. However the observed variation in $^{30}N_2$ fraction was not so simple in the first 5-hr period, and was quite different from that in the $^{29}N_2$ fraction. This complexity must be caused by the concurrent displacement process. Therefore the result should be analyzed first for the displacement process referring to the atomic fraction of ^{15}N in the gas phase.
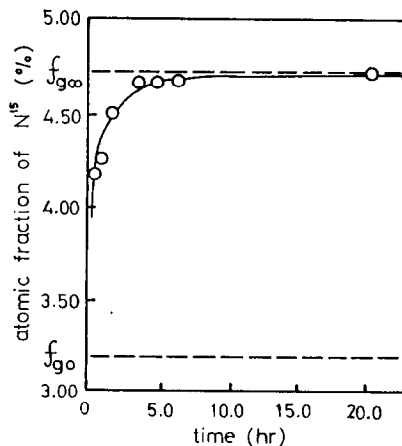

FIG. 2. Time course of the atomic fraction of ^{15}N.

Displacement Process

When we refer to the atomic fraction of ^{15}N it is possible to estimate the rate of the displacement process independently of the isotopic mixing. In Fig. 2, is shown the change in the atomic fraction of $^{15}N(f_g)$ with time, which is calculated from the $^{29}N_2$ and $^{30}N_2$ fractions in Fig. 1, where f_{g0} and $f_{g\infty}$ are the values of f_g at time zero and at time infinity. If there was no displacement, f_g must remain at f_{g0}. The value of $f_{g\infty}$ is calculated supposing that all the preadsorbed nitrogen is displaced. It is shown in Fig. 2 that the value of f_g reached a plateau in about 5 hr, which means that the equilibrium of the displacement process was established. It is to be noted that the plateau value of f_g agrees with the calculated value of $f_{g\infty}$. Hence it may be concluded that all the adsorbed nitrogen is displaceable within about 5 hr.

In order to evaluate the rate of the displacement process a kinetic study has been made. In the experiment as described, the equilibrium of the adsorption had been established prior to the circulation of isotopic nitrogens, so that the rate of adsorption was equal to that of desorption. Let V be the number of molecules being adsorbed or desorbed per unit time. The rate of increase in the number of ^{15}N atoms in the gas phase can be written as the difference between the rates of desorption and adsorption of ^{15}N, as follows:

$$\frac{d}{dt}(2n_g f_g) = 2n_g \frac{df_g}{dt} = 2V(f_s - f_g) \quad (2)$$

where n_g is the number of nitrogen molecules in the gas phase, and f_g and f_s are, respectively, the atomic fractions of ^{15}N in gas phase and adsorbed phase. The total number of ^{15}N atom (N^*) in this reaction system is constant, i.e.,

$$2(n_g f_g + n_s f_s) = N^* = \text{const} \quad (3)$$

where n_s is the number of the nitrogen molecules in the adsorbed phase. Using Eq. (3), Eq. (2) is integrated to give the rate expression

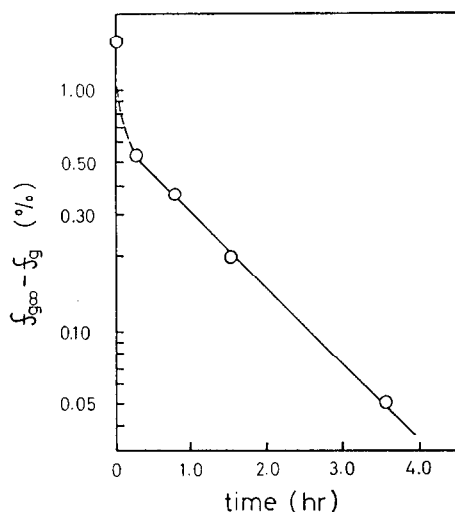$$Vt = -2.3 \frac{n_g n_s}{n_g + n_s} \log \frac{(f_{g\infty} - f_g)}{(f_{g\infty} - f_{g0})} \quad (4)$$

FIG. 3. Plot of $f_{g\infty} - f_g$ as a function of time in connection with Eq. (4).

Since this equation does not assume any mechanism of the displacement process, if the adsorbed state is homogeneous on the iron catalyst so that the every adsorbed nitrogen is displaced with an equal rate of V, the value of $\log(f_{g\infty} - f_g)$ should decrease linearly with time as predicted by Eq. (4). However as seen in Fig. 3 the plot of $\log(f_{g\infty} - f_g)$ vs. t is undoubtedly curved. It may be concluded that the adsorbed nitrogen is inhomogeneous.

As can be seen in Figs. 2 and 3 the rate of the displacement was so fast in the initial stage that the extent of approach to the equilibrium defined by $(f_g - f_{g0})/(f_{g\infty} - f_{g0})$ reached about 0.8 in 1 hr, while it gradually decreased with time as indicated by the curved plot on Fig. 3. An averaged value of V for the later stage of the displacement may be evaluated from the slope of the straight line shown on Fig. 3 to be 1.0×10^{19} molecules/min at 380°C; another run at 400°C gave the same value. The value of V for the initial stage is estimated to be larger than 5.0×10^{19} molecules/min at 380° and 400°C.

Isotopic Mixing

The results shown in Figs. 2 and 3 indicate that the isotopic mixing went on even when the isotopic displacement reached equilib-
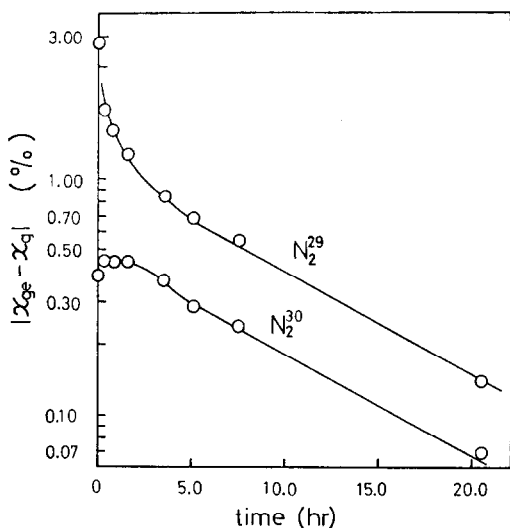
FIG. 4. Plot of $x_g^{30} - x_{ge}^{30}$ and $x_{ge}^{29} - x_g^{29}$ as a function of time in connection with Eqs. (9) and (10).

rium. At this period, the variation of the molecular fraction of $^{29}N_2$ or $^{30}N_2$ was exclusively due to the isotopic mixing reaction. Thus the rate of the mixing can be easily obtained. The rate of decrease of $^{30}N_2$ in the gas phase is given as the difference between the rates of adsorption of $^{30}N_2$ (v_a^{30}) and desorption (v_d^{30}), so that

$$-n_g(dx_g^{30}/dt) = v_a^{30} - v_d^{30} \qquad (5)$$

where x_g^{30} is the fraction of $^{30}N_2$ molecules in the gas phase. The rate of adsorption of $^{30}N_2$ can be written as
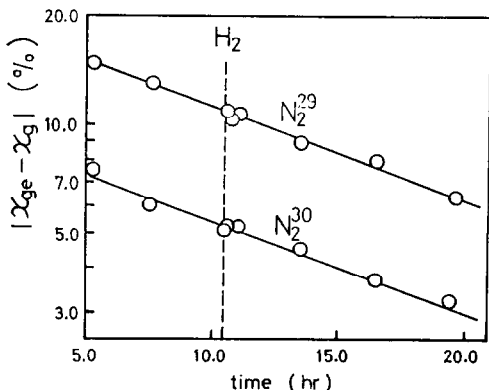

FIG. 5. Plot of $x_g^{30} - x_{ge}^{30}$ and $x_{ge}^{29} - x_g^{29}$ as a function of time in connection with Eqs. (9) and (10). Hydrogen was added to the reaction system at the time which is shown by the broken line.

$$v_a^{30} = Rx_g^{30} \qquad (6)$$

where R is the rate of adsorption or desorption of nitrogen under the adsorption equilibrium which takes part of the isotopic mixing. If it is assumed that the adsorbed nitrogen was dissociated so that the nitrogen desorbing from the surface had statistical distribution with respect to the isotopic species, the rate of desorption of $^{30}N_2$ may be written as

$$v_d^{30} = Rf_s^2 \qquad (7)$$

The rate of decrease of $^{30}N_2$ is therefore given by replacing v_a^{30} and v_d^{30} in Eq. (5) by those in Eqs. (6) and (7)

$$-n_g(dx_g^{30}/dt) = R(x_g^{30} - f_s^2) \qquad (8)$$

f_s varies with time until the isotopic displacement reaches equilibrium, but after that f_s is constant and is equal to f_g. Moreover the square of f_g is equal to the value of x_g^{30} at the equilibrium of the isotopic mixing. Hence in the case of the isotopic displacement being in equilibrium Eq. (8) can be integrated, viz.,

$$Rt = -2.3n_g \log \frac{(x_g^{30} - x_{ge}^{30})}{(x_{g0}^{30} - x_{ge}^{30})} \qquad (9)$$

where x_{ge}^{30} is the value of x_g^{30} at the equilibrium of the isotopic mixing and x_{g0}^{30} is the initial value of x_g^{30}.

In the same manner as above it can be shown that the rate of isotopic mixing is given with the fraction of $^{29}N_2$ (x_g^{29}) as

$$Rt = -2.3n_g \log \frac{(x_{ge}^{29} - x_g^{29})}{(x_{ge}^{29} - x_{g0}^{29})} \qquad (10)$$

According to Eqs. (9) and (10) the rate of adsorption or desorption R is obtainable from the plot of $\log(x_{ge} - x_g)$ against t, which is shown in Fig. 4. The plot is well consistent with Eq. (9) or (10) except while the displacement is occurring. The estimated value of R is 8.8×10^{18} molecules/min at 380°C and from another run 25.6×10^{18} at 400°C.

Effect of Hydrogen

According to Joris and Taylor, the presence of hydrogen in the gas phase accelerates markedly the isotopic mixing. If so, the value

of R must be larger, i.e., the slope of the straight line of Fig. 4 must be steeper, in the presence of added hydrogen than its absence. The experiment was carried out in the same manner as the preceding description but the hydrogen gases which amounted to one-third of the nitrogen were added to the reaction system after 10.5 hr from the start of circulation, resulting the plot of $\log(x_{ge} - x_g)$ vs. t shown in Fig. 5.

As can be seen in this figure, the addition of hydrogen made no change in the slope. It can be therefore concluded that there is no accelerating effect of the added hydrogen such as Joris and Taylor (3) and Kummer and Emmett (4) have reported on doubly promoted iron catalysts.

DISCUSSION

The fact that the plateau value of f_g agrees with the calculated value of $f_{g\infty}$ leads to the conclusion that all the nitrogen in the adsorbed phase is displacable in a few hours.

However the rate of displacement, V, was not equal with all the nitrogen adsorbed. Some were displaced rapidly to give a value of V higher than R as observed in the early stage of the displacement, whereas the value of V for the later stage was nearly equal to the value of R. It may be reasonable in the later stage that the displacement took place by way of the isotopic mixing. On the other hand in the early stage of the displacement, where V was much larger than R, there must be some other process to effect the displacement without accompanying the isotopic mixing. This inference is confirmed by the run at 350°C, where the rate of isotopic mixing was too slow to be observed, but the displacement proceeded up to about 90% of adsorbed nitrogen within 5 hr. Hence the displacement of undissociated nitrogen should be considered.

The relation of the isotopic mixing to the displacement process is well illustrated with following mechanism:

$$N_2(g) \underset{}{\overset{I}{\rightleftharpoons}} N_2(a) \underset{}{\overset{II}{\rightleftharpoons}} 2N(a) \qquad (11)$$
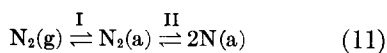
where it is assumed that the isotopic mixing

is caused by the dissociative adsorption of nitrogen. The rate of process II can be measured as R, while the value of V represents the rate of process I or II, depending upon the relative rates of processes I and II. When rate I is larger than rate II the value of V should be larger in the early stage of the displacement than in the later stage, until a substantial part of $N_2(a)$ is displaced. In the later stage of the displacement where the larger part of $N_2(a)$ is isotopically equilibrated with the gas phase, the displacement is controlled by the rate of the process II, and thus the value of V coincides with that of R. This was the case observed. On the other hand, when the rate I is smaller than the rate II, the value of V should agree with that of R through the whole period of the displacement, a time course which was not observed.

Hence the result observed in this work strongly suggests the existence of an undissociated state of adsorbed nitrogen being rapidly displaced with gaseous nitrogen.

Since about 80% of the adsorbed nitrogen was displaced within 1 hr at 380°C, as seen in Fig. 2, the larger part of the adsorbed nitrogen seems to be undissociated at this temperature. At a lower temperature, 350°C, it is similarly concluded that almost all the adsorbed nitrogen is undissociated.

The accelerating effect of the added hydrogen for the isotopic mixing has been reported by several investigators employing promoted iron catalysts. But in the experiment reported here there was no such effect over the unpromoted iron catalyst. It is not obvious what caused the difference.

REFERENCES

1. SCHOLTEN, J. J. F., ZWIETERING, P., KONVALINKA, J. A., AND DE BOER, J. H., Trans. Faraday Soc. 55, 2166 (1959).
2. TAKEZAWA, N., AND EMMETT, P. H., Shokubai 6, 321 (1964).
3. JORIS, G. G., AND TAYLOR, H. S., J. Chem. Phys. 7, 893 (1939).
4. KUMMER, J. T., AND EMMETT, P. H., J. Chem. Phys. 19, 289 (1951).
5. McGEER, J. P., AND TAYLOR, H. S., J. Am. Chem. Soc. 73, 2743 (1951).