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Activation of Nitrogen by Alkali Metal-Promoted Transition Metal

II. Isotopic Exchange in Molecular Nitrogen Over Potassium-Promoted Ruthenium–Carbon Catalyst

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The isotopic exchange in nitrogen has been investigated over the potassium-promoted ruthenium–carbon catalysts between 220 and 300°C. The reaction readily takes place in this temperature range with rate R given by

$$R = \mathrm{A}\exp(-22\,000 \sim -23\,000/RT)P^{1/2}.$$

From the ^{15}N tracer experiment, all the adsorbed nitrogen was proved to be displaceable by the gas phase nitrogen. A slight retardation of the exchange rate is observed in the presence of hydrogen. The exchange rate and the ammonia synthesis rate are of the same magnitude.

INTRODUCTION

It has been reported that the rate of ammonia synthesis over transition metals is remarkably enhanced by addition of alkali metal, particularly when the metals are supported by active carbon (*1–3*). Since the most difficult process for the ammonia synthesis is accepted to be the dissociation of nitrogen molecule, it is expected that the enhancement is also found in the isotopic exchange in nitrogen which requires the dissociation. The present paper deals with the isotopic exchange over the potassium-promoted ruthenium–carbon which gives the highest activity for the ammonia synthesis.

EXPERIMENTAL METHODS

The apparatus was a closed circulating system comprising a reactor. 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.

Ruthenium catalyst supported on active carbon (Tsurumi coal; the BET surface area was about 1000 m^2/g) was prepared by impregnation method from aqueous chloride solution, reduced by circulating hydrogen at 400°C for 65 hr and subjected to adsorption of potassium vapor at 400°C followed by circulation of helium to distribute the potassium metal among the catalyst particles.

The catalysts and their amounts used are as follows:

Catalyst	Amount (g) ($RuCl_3$ + carbon)	K content (wt%)	Character of expt
A	5	7.1	Displacement
B	3	17.3	Exchange
C	3	8.1	Exchange, NH_3 synthesis

Ruthenium content was commonly 5 wt% as metal. CO chemisorption value was 1.3 ml(STP)/g for 5 wt% ruthenium–carbon without potassium.

RESULTS AND DISCUSSION

1. *Displacement of Adsorbed Nitrogen with Gas Phase Nitrogen*

In order to examine whether the adsorbed nitrogen is displaceable by the gas phase nitrogen and participatable for the isotopic exchange, the following experiment (*4*) was carried out.

The ordinary nitrogen $^{28}N_2$ was introduced into the part of circulating system which involved the reactor and was adsorbed on catalyst A until an equilibrium was established under 300 mm Hg at 300°C. The amount of $^{28}N_2$ adsorbed was 1.53 ml(STP)/g-cat. The ^{15}N enriched nitrogen (atomic fraction of ^{15}N; $^{15}f = 68.4\%$) was introduced into the other part of circulating system up to the pressure equal to the equilibrium pressure (300 mm Hg) of the ordinary nitrogen. Then these two parts of gases were connected and circulated through the reactor. The change in the isotopic composition of the circulating gas with time was measured by intermittent sampling.

The time courses of the changes in the mole fractions ^{28}X, ^{29}X and ^{30}X for $^{28}N_2$, $^{29}N_2$ and $^{30}N_2$, respectively, and in the atomic fraction ^{15}f of ^{15}N in the gas phase are shown in Fig. 1, where $^{15}f_0$ and $^{15}f_\infty$ are the values of ^{15}f at time zero and on the complete displacement including all the adsorbed nitrogen, respectively, and $^{i}X_e$ ($i = 28,29,30$) is the value of ^{i}X expected at the exchange equilibrium for all the adsorbed nitrogen in the system.

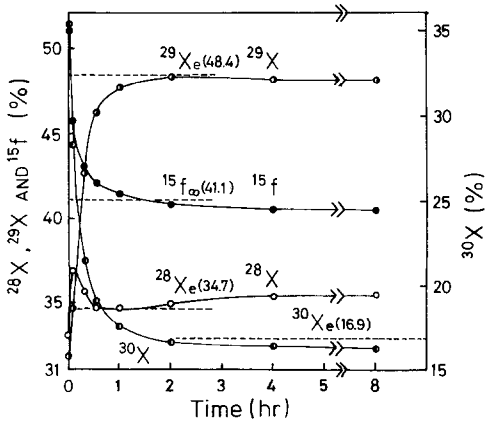

FIG. 1. Time courses of the mole fraction of $^{28}N_2$, $^{29}N_2$ and $^{30}N_2$(^{28}X, ^{29}X and ^{30}X) and of the atomic fraction of ^{15}N in the gas phase (^{15}f) in the displacement run on catalyst A at 300°C. Dotted lines are $^{i}X_e$ or $^{15}f_\infty$.

The time course of ^{28}X clearly reflects the experimental conditions in which only the gas phase contains ^{15}N in the initial condition. The ^{28}X initially increases with time because of the fast desorption of $^{28}N_2$ molecules from the adsorbed phase, while $^{28}N_2$ is concurrently consumed by the isotopic exchange. Thus ^{28}X reaches a maximum after a while (about 10 min) of increase and decreases down to the exchange equilibrium in about 2 hr, whereas ^{30}X monotonously decreases with time because both the adsorption of $^{30}N_2$ and the isotopic exchange give rise to decrease in ^{30}X. It is clear that this catalyst is so active for the isotopic exchange as to result in the equilibrium within 2 hr at 300°C.

On the other hand, ^{15}f solely depends on the displacement process. Thus the displacement results in a decrease in ^{15}f from $^{15}f_0$ (51.1%) down to a plateau value in about 2 hr and the plateau value is approximately in agreement with $^{15}f_\infty(41.1\%)$. From this fact it is concluded that all the adsorbed nitrogen is displaceable under 300 mm Hg at 300°C.

The rate of displacement of adsorbed nitrogen (v) may be estimated from the time course of ^{15}f according to the equation (*4*)

$$-\log \frac{(^{15}f - {}^{15}f_\infty)}{(^{15}f_0 - {}^{15}f_\infty)} = \frac{N_g + N_a}{2.3N_gN_a} vt, \qquad (1)$$

where N_g and N_a are, respectively, the number of nitrogen molecules in the gas phase and in the adsorbed phase. From the data shown in Fig. 1 a value of v at 300°C is obtained at 2.6×10^{19} molecules/min, or 5.2×10^{18} molecules/min, g-cat.

2. *Kinetics of the Isotopic Exchange*

If the isotopic concentration in the gas phase is equal to that in the adsorbed phase, the rate of isotopic exchange (*4*), R (molecules/min), is expressed by

$$-\log\frac{({}^{i}X_e - {}^{i}X)}{({}^{i}X_e - {}^{i}X_0)} = \frac{R}{2.3\mathrm{N_g}}t, \tag{2}$$

where ${}^{i}X$, ${}^{i}X_0$ and ${}^{i}X_e$, are, respectively, the mole fractions of ${}^{i}N_2$ at time t, zero and the equilibrium. R also gives the equalized rate of dissociative adsorption–desorption of nitrogen under the reaction condition. $\mathrm{N_g}$ is the number of nitrogen molecules in the gas phase.

a. Temperature Dependence

The isotopic mixture (${}^{15}f = 30\%$) of nitrogen was adsorbed on catalyst B until an equilibrium was established under 250 mm Hg then circulated. The change in the isotopic composition of the circulating gas with time was measured by continuous sampling.

Log (${}^{29}X_e$–${}^{29}X$) for the runs between 220 and 280°C are plotted against time as shown in Fig. 2. The each value of R can be determined from the slope of the each straight line as shown by Eq. (2). The apparent activation energy of the isotopic exchange is estimated from the Arrhenius plots of R (Fig. 3) to be 22.1 kcal/mole. Similarly on catalyst C the apparent activation energy is also estimated to be 23.2 kcal/mole under 200 mm Hg between 220 and 280°C (Fig. 3).

b. Pressure Dependence

Log (${}^{29}X_e$–${}^{29}X$) for the runs on catalyst B between 50 and 250 mm Hg at 280°C are plotted against time as shown in Fig. 4. Figure 5 shows the effect of the nitrogen pressure on the exchange rate. From the slope of the straight line in Fig. 5, the exchange rate is found to be pro-

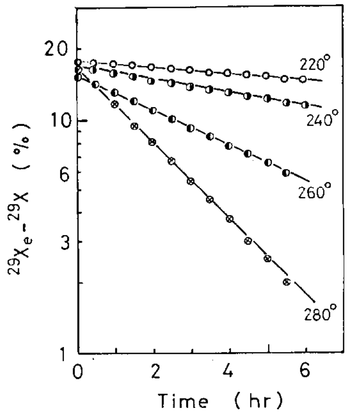

FIG. 2. Log plots of (${}^{29}X_e$–${}^{29}X$) as a function of time at various temperatures on catalyst B under 250 mm Hg N_2.

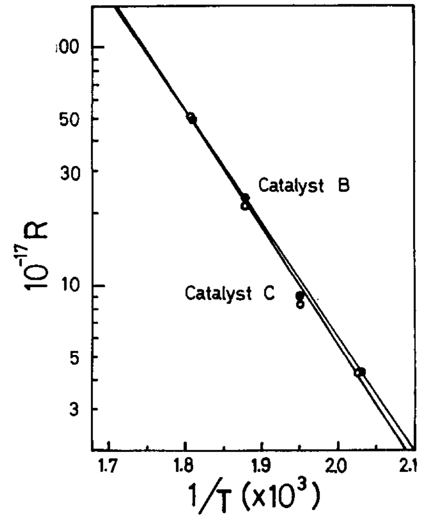

FIG. 3. Arrhenius plots of the exchange rate R on catalyst B under 250 mm Hg (●) and on catalyst C under 200 mm Hg (○).

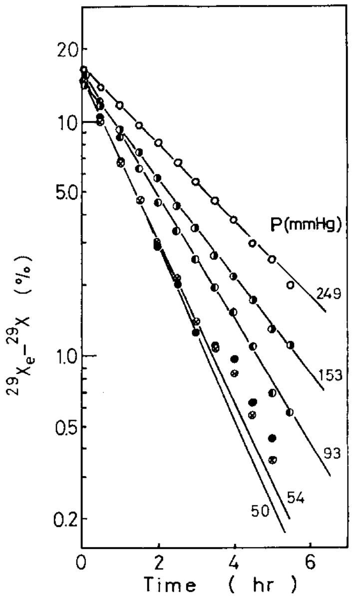

FIG. 4. Log plots of (${}^{29}X_e$–${}^{29}X$) as a function of time under various pressures of nitrogen on catalyst B at 280°C.

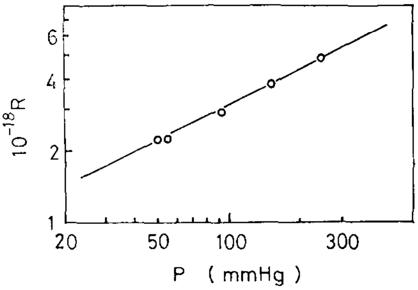

FIG. 5. Nitrogen pressure dependence of the exchange rate R estimated from the results in Fig. 4.

portional to one-half power of the nitrogen pressure. Similarly on catalyst C it was confirmed that the apparent reaction order is about one half.

The above results can be expressed by the equation

$$R = 1.8 \times 10^{26} \exp(-22\,100/RT)P^{1/2}, \quad (3)$$

for the catalyst B.

The one-half order dependence of the exchange rate has been reported over Fe, Fe–Al_2O_3 and Fe–Al_2O_3–K_2O by Boreskov, Gorbunov and Masanov (*5*), Schultz *et al.* (*6*) and Takezawa and Toyoshima (*7*). The one-half order dependence may be interpreted in terms of adsorption constant K of nitrogen in the expression

$$\text{rate} = \frac{kP_{N_2}}{[1 + (KP_{N_2})^{1/2}]^2}. \quad (4)$$

When K has a certain value, the above expression might be approximated to

$$\text{rate} = k'P_{N_2}{}^{1/2}. \quad (5)$$

If this is the case, the rate should be proportional to P_{N_2} at high temperature or under very low pressure of P_{N_2}. Furthermore the values of K on ruthenium should be much smaller than on iron. In this respect, the fact that the reaction order of the isotopic exchange on ruthenium is again one half as on iron seems to rule out the above interpretation. It should be pointed out that the above interpretation is also inconsistent with the previous conclusion (*8*) that the surface coverage of nitrogen on ruthenium is very small. Thus there should be a certain mechanism to give the characteristic one-half order. Clarification of this problem should be subjected to a further work.

c. *Comparison of the Rate of Isotopic Exchange with the Rate of Displacement*

The rate of displacement was determined on catalyst A (K content 7.1 wt%) under 300 mm Hg at 300°C to be 5.2×10^{18} molecules/min, g-cat as mentioned already. On the other hand, the rate of isotopic exchange under the same conditions may be estimated from the results on the catalyst C (K content 8.1 wt%) according to the temperature and pressure dependence to be 4.0×10^{18} molecules/min, g-cat (Fig. 3). Both values are fairly in agreement. From this result, the atomic state of adsorption is suggested. But some part of adsorbed nitrogen can be molecular, because this result is also consistent with the case where the rate of surface exchange between molecular and atomic species is faster than the rate of displacement.

d. *Isotopic Exchange Over Ruthenium–Carbon*

No adsorption of nitrogen occurred on 5 wt% ruthenium–carbon (catalyst C without potassium) under 250 mm Hg at 280°C and the isotopic exchange hardly proceeded in 4 hr at 400°C. Interestingly no ammonia is formed on the ruthenium–carbon without potassium at 400°C as previously reported (*1*). It is clear that the addition of alkali metal to ruthenium–carbon simultaneously activates for the ammonia synthesis and for the isotopic exchange in nitrogen. This is quite reasonable as expected in the introduction.

3. Isotopic Exchange in the Presence of Hydrogen

Hydrogen was added to the reaction system during a run of isotopic exchange in nitrogen under 250 mm Hg at 240 and 280°C. The amount of added hydrogen was about one third of nitrogen. The resulting plots of $({}^{29}X_e - {}^{29}X)$ vs time are shown in Fig. 6, where the arrow shows the time when hydrogen was added.

As soon as hydrogen was added, the

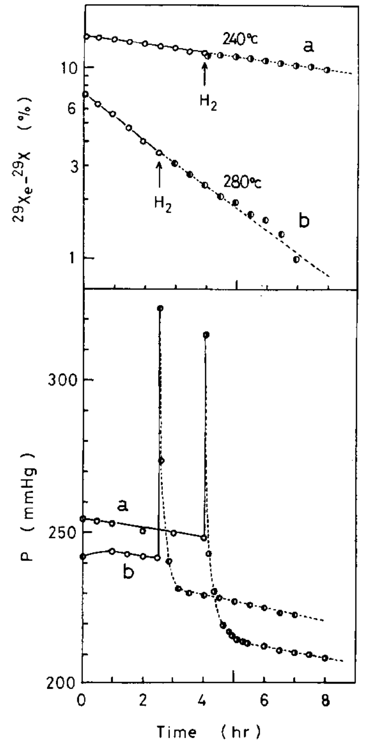

FIG. 6. The effect of hydrogen on the exchange rate on catalyst B under 250 mm Hg N_2 at 240 and 280°C. The amount of hydrogen was about ⅓ of nitrogen.

total pressure of the reaction system rapidly decreased. In about 1 hr all the added hydrogen and a part of the nitrogen in the gas phase were adsorbed. No hydrogen was detected in the gas phase by mass spectrometric analysis. Although the nitrogen pressure was decreased by the addition of hydrogen and thus the slope should increase on the basis of one-half order dependence on nitrogen pressure, the slope of the line in Fig. 6 does not change at 240°C and is slightly lowered at 280°C. That is, the isotopic exchange is slightly retarded by the presence of hydrogen. The extent of retardation for the apparent rate constant is about 8% at 240°C and 15% at 280°C.

In relation to the mechanism of ammonia synthesis, it is important to compare the exchange rate with that of ammonia synthesis. The ammonia synthesis rate was obtained on catalyst C from rate of volume decrease of circulating N_2–H_2 stoichiometric mixture under a stationary state and constant pressure 600 mm Hg. The apparent activation energy for the synthesis was estimated from the Arrhenius plots of the synthesis rate between 220 and 280°C to be 23.8 kcal/mole. This value is in agreement with that for the isotopic exchange (23.2 kcal/mole). The above two rates are compared in mole ammonia basis in Fig. 7 as functions of temperature under a common nitrogen pressure of 150 mm Hg. The rate of isotopic exchange in mole nitrogen is made twice to $V(R)$. Since the apparent activation energy is about the same for both reactions, as mentioned above, the two lines are parallel. Although both rates are similar in magnitude, V(R) is about two times as large as the synthesis rate V. In view of the negative effect of hydrogen on the exchange rate, the real $V(R)$ of the stoichiometric mixture and its difference from the synthesis rate would be smaller.

Such agreements in the value of activation energies and the magnitude of the rates are consistent with the rate determining dissociation of nitrogen molecule in the ammonia synthesis if the surface

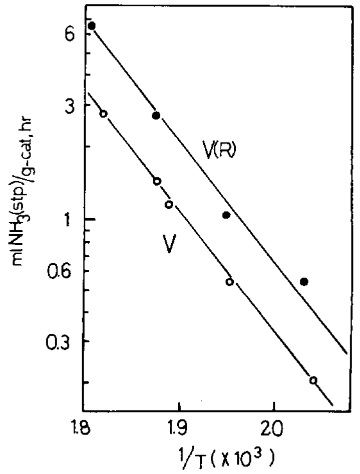

FIG. 7. Comparison of the exchange rate with the ammonia synthesis rate in mole ammonia basis as functions of temperature under a common nitrogen pressure of 150 mm Hg on catalyst C.

coverage by nitrogen is commonly small in both reactions as previously estimated (*8*). However the observed one-half order kinetics of the exchange rate cannot be understood on this basis. There seems to be a key to the mechanism of activation of nitrogen molecule.

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