

Activation of Nitrogen by Alkali Metal-Promoted Transition Metal

VI. Hydrogen Effect on Isotopic Equilibration of Nitrogen and Rate-Determining Step of Ammonia Synthesis on Potassium-Promoted Ruthenium Catalysts

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The effect of hydrogen on isotopic equilibration of nitrogen was studied on ruthenium catalysts with and without potassium at $P_{N_2} = 40-150$ mm Hg, $P_{H_2} = 7-180$ mm Hg and 300-450°C. The equilibration rate is increased on pure Ru but is decreased on Ru-K by the addition of hydrogen. The rate of ammonia synthesis is correspondingly faster than equilibration on pure Ru but is slower on Ru-K. The equilibration rate on Ru-K is decreased by condensing the ammonia produced in the presence of hydrogen and by increasing the H_2/N_2 ratio and approaches negligible value at $H_2/N_2 = 3$, demonstrating that the rate-determining step of ammonia synthesis is the dissociation of nitrogen molecule. The equilibration rate on Ru-K in the presence of ammonia also decreases as hydrogen pressure increases, whereas the reaction order with respect to nitrogen pressure is higher than that in the absence of hydrogen, suggesting that the adsorbed hydrogen exhibits a retarding effect on the adsorption of nitrogen. The surface area of Ru-K was found to increase on hydrogen treatment of nitrogen covered surface, suggesting a corrosive adsorption of nitrogen to form a nitride on Ru-K.

INTRODUCTION

It has been shown that the potassium-promoted ruthenium efficiently catalyzes the isotopic equilibration of nitrogen (1) as well as the ammonia synthesis (2). In the preceding paper (3) it was revealed that the addition of potassium enhances the adsorption strength of nitrogen on ruthenium. In conformity with this, an intense ir absorption spectrum of nitrogen was found on Ru-Al₂O₃-K (4). It was also shown that the rate of isotopic equilibration of nitrogen over Ru-A.C (active carbon)-K (1) is retarded by the presence of hydrogen, in contrast to the behavior of a doubly promoted iron catalyst. Further investigation of this hydrogen effect seemed

important in relation to the mechanism of nitrogen activation. The present paper deals with the kinetics of isotopic equilibration of nitrogen in the presence of hydrogen over potassium-promoted ruthenium catalysts.

EXPERIMENTAL METHODS

Catalysts. Five ruthenium catalysts were used as follows; Ru (1.6 g), Ru-K (1.6 g; K, 0.24%*), Ru-Al₂O₃ (Ru 0.5 wt%, 10 g), Ru-Al₂O₃-K (Ru 0.5 wt%, 10 g; K, 0.5%*), and Ru-A.C-K (Ru 5 wt%, 1.5 g; K, about 15%). The first four catalysts were the same samples as used in the preceding paper (3) and Ru-A.C-K was prepared in the same manner as previously

done (1). A large part of the kinetic measurements was made with Ru-K, which exhibited a stable activity in repeated runs made in a period of more than 1 yr.

Apparatus and procedure. The apparatus was a closed circulating system of about 85 ml with a U-tube containing the catalyst, connected to a manometer, a gas burette and a quadrupole mass spectrometer which permitted continuous analyses of the circulating gas. The isotopic mixture of nitrogen gas (^{15}N , about 20 at.%) was preadsorbed on the catalyst at the reaction temperature until an adsorption equilibrium was established under the reaction pressure. The isotopic equilibration was carried out by circulating nitrogen gas through the reactor. The change in the isotopic composition of circulating gas with time was continuously followed by mass spectrometry. The equilibration rate, R (molecules/min), was determined from the first order plot of $^{29}\text{N}_2$ mole fraction according to Eq. (1):

$$-\log \frac{(^{29}X_e - ^{29}X)}{(^{29}X_e - ^{29}X_0)} = \frac{R}{2.3N_g} t, \quad (1)$$

where ^{29}X , $^{29}X_0$, and $^{29}X_e$ are, respectively, the mole fraction of $^{29}\text{N}_2$ at time t , zero and equilibrium. N_g is the number of nitrogen molecules in the gas phase.

The kinetics of isotopic equilibration in the presence of hydrogen was determined as follows: First the hydrogen of prescribed pressure was introduced to the reaction system where the adsorption of nitrogen had been in equilibrium. The equilibration rate in the presence of hydrogen was determined from the change of ^{29}X with time as described above. The amounts of adsorption of nitrogen and hydrogen were so small on Ru-K, in contrast to those on active carbon-supported catalyst (1), that the change in hydrogen pressure due to adsorption was negligible. For example, the amount of nitrogen adsorption on Ru-K (300°C, 19 hr) was 0.4 ml (STP)/

1.6 g, being 2% of the total nitrogen in the reaction system. The pressure decrease of nitrogen due to the production of gaseous ammonia in the presence of hydrogen was less than 1%. The equilibration rate was also determined during ammonia synthesis by removing ammonia with a liquid nitrogen trap. For measurements in the absence of hydrogen after a run in the presence of hydrogen, the gas phase was first displaced by nitrogen and then the adsorbed hydrogen was removed as ammonia by circulating nitrogen with liquid nitrogen trap at 300–350°C. In this way the hydrogen-free surface was reproduced. The ammonia synthesis rate was obtained on the same catalyst from the rate of volume decrease of a circulating stoichiometric mixture of N_2 and H_2 under a stationary state and constant pressure of 600 mm Hg, where the stationary state of reaction was confirmed by the rate of increase in the amount of trapped ammonia.

RESULTS

1. The Effect of Added Hydrogen on the Isotopic Equilibration of Nitrogen and the Ammonia Synthesis Rate

The effect of added hydrogen on unsupported Ru and Ru- Al_2O_3 with and without potassium are shown in Figs. 1 and 2, as $\log(^{29}X_e - ^{29}X)$ -time plot according to Eq. (1). Since the equilibration

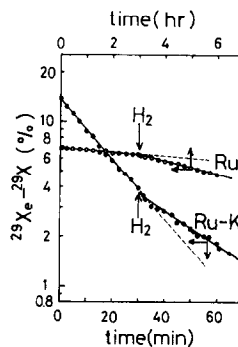


FIG. 1. Effect of added hydrogen on equilibration rate (Ru, 450°C; Ru-K, 380°C).

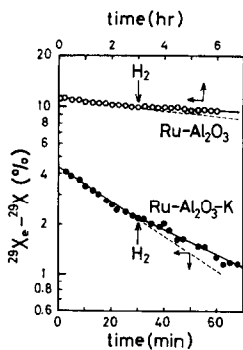


FIG. 2. Effect of added hydrogen on equilibration rate (Ru-Al₂O₃, 450°C; Ru-Al₂O₃-K, 310°C).

rate should be given by slope of plots in Figs. 1 and 2, the hydrogen effect may be expressed by the ratio of slope as shown in Table 1. It is to be noted that on Ru catalysts *with potassium* the addition of hydrogen decreases the equilibration rate irrespective of the support and of supported or unsupported, whereas it increases the rate on pure ruthenium. Ru-Al₂O₃ behaves differently from ruthenium. The addition of hydrogen decreases the rate of equilibration as observed on Fe-Al₂O₃ (5).

A comparison was made between the rate of ammonia synthesis and that of isotopic equilibration on the same Ru catalyst. The Arrhenius plots of the equilibration rate under 150 mm Hg and the ammonia synthesis rate under 600 mm Hg (H₂/N₂ = 3) on unsupported ruthenium with and without potassium are shown in Fig. 3, where both rates are commonly

TABLE 1

Effect of Hydrogen on the Equilibration Rate

Catalyst	Temp (°C)	N ₂ pressure (mm Hg)	Added H ₂ pressure (mm Hg)	R _H /R
Ru	450	150	52	2.5
Ru-K	380	150	48	0.6
Ru-Al ₂ O ₃	450	151	53	0.5
Ru-Al ₂ O ₃ -K	310	150	35	0.6
Ru-A.C-K	280	240	80	0.85
[Ref. (1)]				

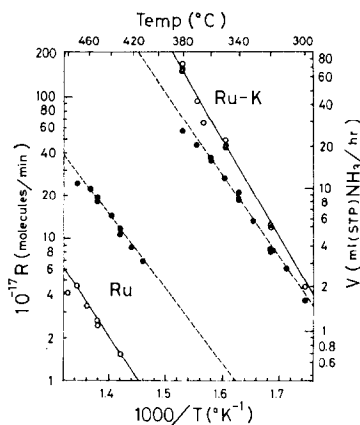


FIG. 3. Enhancement of rates of isotopic equilibration and of ammonia synthesis by addition of potassium to ruthenium (○) isotopic equilibration, $P_{N_2} = 150$ mm Hg; (●) ammonia synthesis, $P_{N_2+3H_2} = 600$ mm Hg.

expressed in numbers of nitrogen molecules (left ordinate) and in numbers of corresponding ammonia molecules (right ordinate). It is clear that the addition of potassium to pure ruthenium dramatically activates both reactions, and that the extent of enhancement is more remarkable in the isotopic equilibration (about 480 times at 400°C) than in the ammonia synthesis (about 25 times at 400°C). It is also found that the rate of ammonia synthesis is faster than that of equilibration on pure ruthenium but is slower on Ru-K. This fact is consistent with the effect of hydrogen on the rate of isotopic equilibration which is increased on pure ruthenium but is decreased on Ru-K by introducing hydrogen into the reaction mixture of nitrogen as shown in Fig. 1.

2. Kinetics of the Isotopic Equilibration in the Presence of Hydrogen and the Equilibration Rate during Ammonia Synthesis

The hydrogen pressure dependence of equilibration rate at 320°C under a constant nitrogen pressure (60 mm Hg) is shown by first order plots of ²⁹N₂ mole fraction in Fig. 4a. The equilibration rates

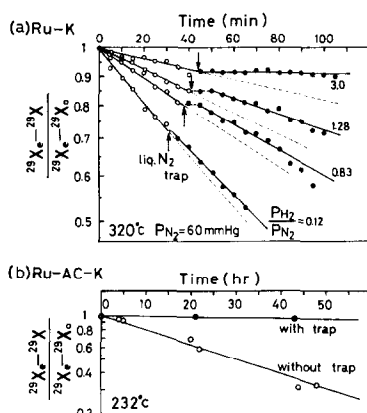


FIG. 4. Isotopic equilibration of nitrogen in the presence of hydrogen and during ammonia synthesis. (a) Ru-K, 320°C, $P_{N_2} = 60$ mm Hg; (b) Ru-A.C-K, 232°C, (\bullet) $P_{N_2} = 85$ mm Hg, $P_{H_2}/P_{N_2} = 5$; (\circ) $P_{N_2} = 22$ mm Hg, $P_{H_2}/P_{N_2} = 2.5$.

as determined from the slope of each straight line are plotted as a function of hydrogen pressure in Fig. 5. It is found that the equilibration rate on Ru-K decreases as the hydrogen pressure increases corresponding to a reaction order with respect to P_{H_2} of about -0.4 .

The arrows in Fig. 4a show the time when a liquid nitrogen trap was set to remove the formed ammonia. It is clearly seen that as soon as the ammonia is removed by condensation, the equilibration rate changes to a lower one which also decreases as H_2/N_2 ratio increases and ultimately becomes immeasurably small at about $H_2/N_2 = 3$. The same result was observed on Ru-A.C-K at 232°C as

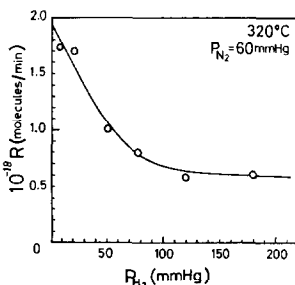


FIG. 5. Rate of equilibration as a function of hydrogen pressure (320°C, $P_{N_2} = 60$ mm Hg).

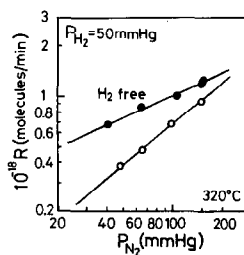


FIG. 6. Rates of equilibration as functions of nitrogen pressure with and without hydrogen (320°C, $P_{H_2} = 50$ mm Hg).

shown in Fig. 4b. The isotopic equilibration observed in the absence of liquid nitrogen trap can not be observed in the presence of the trap. These results demonstrate that, once nitrogen is chemisorbed, it is quickly hydrogenated to ammonia in the presence of hydrogen so that the isotopic equilibration is substantially suppressed. This means that the rate-determining step of ammonia synthesis is the dissociation of nitrogen molecule on Ru-K as well as on Ru-A.C-K. However, since the isotopic equilibration does proceed even with trapping ammonia if the hydrogen pressure is lower, it appears that the hydrogenation of chemisorbed nitrogen is not extraordinarily fast.

The nitrogen pressure dependence of equilibration rate at 320°C under a constant hydrogen pressure of 50 mm Hg was determined as shown in Fig. 6 together with the result in the absence of hydrogen (3). It is seen that the presence of hydrogen causes the reaction order with respect to nitrogen pressure to increase from 0.44 to 0.85. Moreover, the reaction order in the presence of hydrogen (50 mm Hg) was almost unity at 350°C. If the retardation of isotopic equilibration by hydrogen is caused by an adsorbed species such as $NH_x(a)$, the reaction order in P_{N_2} would remain fractional even in the presence of hydrogen, because the increase in nitrogen pressure would increase the amount of $NH_x(a)$. Hence it is assumed that nitrogen and hydrogen are adsorbed separately on

the same surface. If the Langmuir equation for the dissociative adsorption is applied, the equilibration rate in the presence of hydrogen without trap, R_H , may be given by

$$R_H = \frac{kP_{N_2}(1 - \theta_N - \theta_H)^2}{[1 + (K_N P_{N_2})^{\frac{1}{2}} + (K_H P_{H_2})^{\frac{1}{2}}]^2} \quad (2)$$

where k , θ_N , θ_H , K_N , K_H , P_{N_2} , and P_{H_2} are, respectively, rate constant, surface coverages of nitrogen and hydrogen, adsorption constants for nitrogen and hydrogen and partial pressures of nitrogen and hydrogen. The Eq. (2) is transformed as follows:

$$\frac{1}{(R_H)^{\frac{1}{2}}} = \frac{1 + (K_N P_{N_2})^{\frac{1}{2}}}{(k P_{N_2})^{\frac{1}{2}}} + \left(\frac{K_H P_{H_2}}{k P_{N_2}} \right)^{\frac{1}{2}} \quad (3)$$

$$\left(\frac{P_{N_2}}{R_H} \right)^{\frac{1}{2}} = \frac{1 + (K_H P_{H_2})^{\frac{1}{2}}}{k^{\frac{1}{2}}} + \left(\frac{K_N P_{N_2}}{k} \right)^{\frac{1}{2}} \quad (4)$$

The results in Figs. 5 and 6 are examined by plots of $1/(R_H)^{\frac{1}{2}}$ vs $(P_{H_2})^{\frac{1}{2}}$ and of $(P_{N_2}/R_H)^{\frac{1}{2}}$ vs $(P_{N_2})^{\frac{1}{2}}$, respectively, as shown in Figs. 7 and 8. The linear relations as shown suggest that the effect of hydrogen can be understood by the assumed model.

Since the rate of equilibration in the absence of hydrogen is, as previously reported (3), expressed by

$$R = \frac{kP_{N_2}}{[1 + (K_N P_{N_2})^{\frac{1}{2}}]^2} \quad (5)$$

the values of k , K_N , and K_H at 320°C are determined for the absence and presence of hydrogen as follows:

	Absence of H ₂	Presence of H ₂
k (molecules/min mm Hg N ₂)	5.8 ×10 ¹⁶	3.5 ×10 ¹⁶
K_N (mm Hg N ₂ ⁻¹)	1.9 ×10 ⁻²	2.2 ×10 ⁻³
K_H (mm Hg H ₂ ⁻¹)	—	1.1 ×10 ⁻²

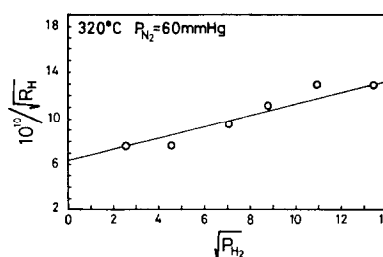


FIG. 7. Test of Eq. (3) (Ru-K, 320°C, $P_{N_2} = 60$ mm Hg).

It is clear that the hydrogen addition reduces k and K_N values to about three fifths and one tenth of the original values, respectively, and that the adsorption of hydrogen is about fivefold stronger than that of nitrogen in the presence of hydrogen. Thus it is likely that hydrogen takes the place of adsorbed nitrogen by reducing the adsorption strength of nitrogen, giving rise to the higher reaction order with respect to nitrogen.

3. Enlargement of Ru-K Surface by Hydrogen Treatment of Nitrogen Covered Surface

The equilibration activity in the absence of hydrogen was determined after a series of runs in the presence of hydrogen (the isotopic equilibration and the ammonia synthesis) were carried out at 300–400°C. The rate of equilibration at 350°C before (line 1) and after (line 2) those runs in the presence of hydrogen are shown in Fig. 9 as functions of nitrogen pressure. Before those runs of line 2, the adsorbed hydrogen remaining on the catalyst was removed as ammonia by circulating nitrogen (215 mm

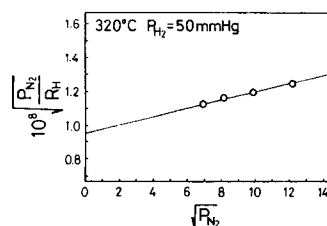


FIG. 8. Test of Eq. (4) (Ru-K, 320°C, $P_{H_2} = 50$ mm Hg).

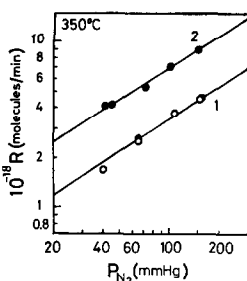


Fig. 9. Nitrogen pressure dependence of equilibration rates before (1) and after (2) the runs with hydrogen (Ru-K, 350°C).

Hg) at 280°C for 24 hr with liquid nitrogen trap. It can be seen from Fig. 9 that the reaction order with respect to P_{N_2} is reverted by the removal of adsorbed hydrogen to the original one in the absence of hydrogen, while the activity is increased about twofold. The activity change is shown in Fig. 10 as Arrhenius plots of the equilibration rates measured under 150 mm Hg before (line 1) and after (line 2) those runs with hydrogen. It is shown that the activation energy for the equilibration is unchanged at about 32 kcal/mole in spite of the increase in activity (about twofold). Thus the change in the surface area of Ru-K catalyst was examined by BET method using Kr at -195°C without exposing to air. It was found as expected that the surface area was increased from an original value of 1.7 m^2 to 2.7 m^2 after

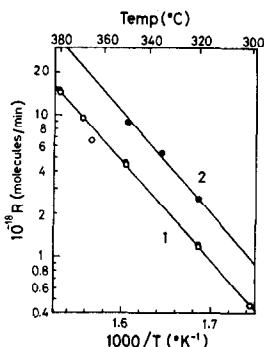


Fig. 10. Arrhenius plots of equilibration rates before (1) and after (2) the runs with hydrogen (Ru-K, $P_{N_2} = 150$ mm Hg).

those runs in the presence of hydrogen (about 1.6 times). Thus the large part of increase in activity can be ascribed to the enlargement of surface area. No further change of activity was, however, observed in the successive runs even by changing the reacting atmosphere.

As can be seen from comparison of Figs. 5 and 6, the equilibration rate in Fig. 5 is about twice as fast as that in Fig. 6 under the same conditions, viz, at 320°C under $P_{N_2} = 60$ mm Hg and $P_{H_2} = 50$ mm Hg. The rate constant of 3.5×10^{16} given before was obtained from the results of Fig. 6 and the results of Fig. 5 give a value of 7.5×10^{16} . Since the runs in Fig. 6 were the first series of runs in the presence of hydrogen, the equilibration activity was seemingly identical with that before the enlargement of surface area, which seemed to take place during the ammonia synthesis runs.

DISCUSSION

1. Effects of Hydrogen

It was found that the effect of added hydrogen on the rate of equilibration was enhancing on Ru while suppressing on Ru-K. The cause of suppression seems to be twofold. Firstly the adsorption constant for nitrogen decreases about one order of magnitude on addition of hydrogen. Secondly the adsorption sites are largely occupied by hydrogen owing to the larger adsorption strength ($K_H/K_N \doteq 5$) so that the number of available sites decreases for nitrogen. Similar effect of hydrogen on the rate of isotopic equilibration was reported by Guyer *et al.* (6) on osmium, where the adsorption of hydrogen was estimated to be one order of magnitude more than that of nitrogen.

The enhancement of isotopic equilibration of nitrogen on ruthenium effected by the addition of potassium has been ascribed to an electron donation from potassium to ruthenium (1, 3). The situation

may change in the presence of hydrogen because it gives rise to ammonia formation. In the presence of ammonia, the metallic potassium would be, at least partly, transformed into potassium amide or imide as suggested on Ru-A.C-K (?). Otherwise the potassium would be partly transformed into hydride in the presence of hydrogen. Anyway such transformation of potassium would result in a decrease of its electron donating ability. The significant decrease in the adsorption constant (K_N) by the addition of hydrogen seems to be caused by such change in potassium. On the other hand on pure ruthenium, those adsorbed species such as NH_x would be favorable by their electron donating nature, thus giving rise to the enhancement of equilibration by the presence of hydrogen.

Another effect of hydrogen was found in the increase of catalyst surface area after a series of runs in the presence of hydrogen, presumably ammonia synthesis runs at higher temperature. Similar phenomenon is well known when a metal is subjected to oxidation followed by reduction. Thus the surface area increase observed on Ru-K seems to be due to a "cultivation" of ruthenium surface caused by reduction of nitrided surface. The strong adsorption of nitrogen as reported in the preceding paper (3) suggests that a nitride can be formed on Ru-K while it is unknown with ruthenium*.

2. The Rate of Isotopic Equilibration during Ammonia Synthesis

The rate-determining step of ammonia synthesis over Ru-K and Ru-A.C-K was demonstrated to be the dissociation of nitrogen by the stop of isotopic equilibration during ammonia synthesis as discussed in Results. However the isotopic equilibration does proceed during ammonia synthesis if the hydrogen pressure is lower, giving an information about the relative rates of elementary steps. The isotopic

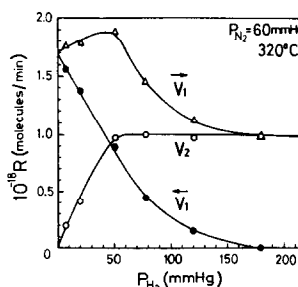
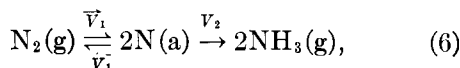


FIG. 11. Relative rates of elementary steps of the ammonia synthesis under a steady state condition (Ru-K, 320°C, $P_{N_2} = 60$ mm Hg).

equilibration and the ammonia synthesis are interrelated by the scheme:



where \bar{V}_1 and \bar{V}_1 are, respectively, the forward and backward rates of nitrogen dissociation and $V_2 (= \bar{V}_2 - \bar{V}_2)$ is the net rate of hydrogenation of adsorbed nitrogen.

Under a stationary condition, those rates are correlated by

$$\bar{V}_1 - \bar{V}_1 = V_2. \quad (7)$$

V_2 is obtained by the rate of ammonia formation. \bar{V}_1 is given by the rate of isotopic equilibration during ammonia synthesis with ammonia being trapped. Thus \bar{V}_1 is given by $\bar{V}_1 + V_2$. These rates are estimated and plotted as functions of hydrogen pressure in Fig. 11. V_2 increases while \bar{V}_1 decreases, as the hydrogen pressure increases, resulting in a maximum of \bar{V}_1 . The first increase in \bar{V}_1 may be ascribed to an increase in available surface caused by the removal of adsorbed nitrogen by hydrogenation and the decrease beyond the maximum should be due to the adsorbed hydrogen, i.e., to the decrease in the number of free sites for nitrogen adsorption.

The increase in \bar{V}_1 due to the removal of adsorbed nitrogen may be estimated on the basis of Eq. (2) for R_H . Under the reaction

condition of R_H determinations, where no liquid nitrogen trap was used, the forward rate of nitrogen chemisorption is limited by the adsorbed nitrogen and thus the forward and backward rates are equalized. The rate in the absence of adsorbed nitrogen ($R_{H'}$) may be estimated by

$$\frac{R_{H'}}{R_H} = \frac{[1 + (K_N P_{N_2})^{\frac{1}{2}} + (K_H P_{H_2})^{\frac{1}{2}}]^2}{[1 + (K_H P_{H_2})^{\frac{1}{2}}]^2}, \quad (8)$$

applying those values of $K_N (2.2 \times 10^{-3})$ and $K_H (1.1 \times 10^{-2})$ obtained already. Under the reaction condition of $P_{N_2} = 60$ mm Hg and $P_{H_2} = 50$ mm Hg, the ratio $R_{H'}/R_H$ is estimated to be 1.5, while the ratio \overline{V}_1/R_H is 1.7. Although the agreement is not so satisfactory, it may be understood that the rate of nitrogen chemisorption is increased by the removal of adsorbed nitrogen, while it is suppressed by the presence of adsorbed hydrogen.

The last conclusion seems important in relation to the ammonia synthesis reaction. Since the ammonia synthesis is to be made in the presence of hydrogen, it implies that the rate-determining chemisorption of nitrogen is suppressed by the adsorbed hydrogen. This seems to give rise to the rather high apparent activation energy of ammonia synthesis (27 kcal/

mole on Ru-K, while 24 kcal/mole on Ru) in spite of the significant enhancement in the catalytic activity.

*Note added in proof. No nitride formation has been recorded (8), while Guyer *et al.* (9) observed that, when treated with ammonia at 300°C, about 3% of ruthenium reacted with nitrogen. Otto and Shelef (10) also found the strongly held nitrogen atoms on ruthenium surface after treatment with NO-NH₃ mixture at 400°C. The potassium contents of Ru-K and Ru-K-Al₂O₃ reported in the previous paper (3) were wrong and are corrected in this paper.

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