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# Nitrogen Equilibration Reaction $^{28}N_2 + {}^{30}N_2 = 2{}^{29}N_2$ Over a Well-Reduced Iron Synthetic Ammonia Catalyst*

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The equilibrium reaction of nitrogen $^{28}N_2 + {}^{30}N_2 = 2{}^{29}N_2$ was studied over an iron synthetic ammonia catalyst which was reduced by hydrogen with excessive precautions. It was found that the rate of the equilibration reaction was proportional to one-half power of the partial pressure of nitrogen and the activation energy was 33 kcal/mole.

Hydrogen was found to exert no influence upon the rate of the reaction above 400°C whereas it accelerated the rate at 351°C.

The results reported here were compared with those obtained by other authors and discussion is presented on the action of the promoter on the catalyst in connection with the states of adsorbed nitrogen.

## INTRODUCTION

Several reports have been published on the nitrogen isotope equilibration reaction $^{28}N_2 + {}^{30}N_2 = 2{}^{29}N_2$ over iron synthetic ammonia catalysts in connection with the study of the states of adsorbed nitrogen and of the mechanism of ammonia synthesis (*1–5*).

More than 30 years ago, Joris and Taylor (*1*) studied the equilibration reaction over the iron synthetic ammonia catalysts, finding that the reaction proceeded extremely slowly near 450 to 500°C but was accelerated by the presence of hydrogen. From these findings, they concluded that nitrogen was predominantly held on the surface of the catalyst as a form of undissociative adsorption $=N—N=$ or $—N{=}N—$ and with the addition of hydrogen it changed into adsorbed imino NH or amino $NH_2$ by breakage of N—N or N=N bond, giving rise to the equilibration reaction.

However, Kummer and Emmett (*2*) and McGeer and Taylor (*3*) showed later that the reaction proceeded at a considerable rate at 450 or 500°C as long as the catalyst was reduced carefully. It was, therefore, concluded that nitrogen was adsorbed dissociatively on the iron synthetic ammonia catalyst. In addition, these authors found that hydrogen accelerated the equilibration reaction; whereas oxygen markedly poisoned the reaction.

Thereafter, the equilibration reaction was also studied by Boreskov *et al.* (*4*) and Gorbunov and Boreskov (*5*) and a similar effect was found with hydrogen on the doubly-promoted iron catalyst.

Tamaru (*6*) studied the nitrogen adsorption and also found the accelerating effect of hydrogen upon the adsorption. However, one of the present authors and Emmett (*7*) recently showed that hydrogen exerted practically no influence upon the adsorption over the iron synthetic ammonia catalysts which were reduced by the highly purified hydrogen.

In view of the facts outlined above, the present study aimed to reexamine the nitrogen equilibration reaction as well as the

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TABLE 1

NITROGEN EQUILIBRATION REACTION $^{28}N_2 + ^{30}N_2 = 2^{29}N_2$ OVER THE DOUBLY-PROMOTED IRON CATALYST REDUCED AT 450°C FOR 50 HR (Series I expts.)

Catalyst used, 2.6 g; surface area, 18.1 $m^2/g$; proportion of the surface covered with: iron; 19.2%; potassium oxide, 26.7%; alumina and/or silica, 55.1%.

| Run | Temp $T$ (°C) | Time $t$ (hr) | $^{29}N_2$ $Z^N$ (%) | $^{29}N_2(e)$ $Z_e^N$ (%) | Vol of nitrogen in gas phase (ml STP) | $P$ (mm Hg) | $V$ (ml STP/hr) | Remarks |
|---|---|---|---|---|---|---|---|---|
| 1 | 433 | 0 | 2.11 | 33.1 | 9.1 | 78 | 8.0 | $H_2$ contained in the system: 0.63 ml STP |
| | | 1.8 | 24.50 | 30.3 | | | | |
| 2 | 433 | 0 | 1.66 | 20.4 | 21.3 | 198 | 9.6 | |
| | | 2 | 12.75 | 20.2 | 20.2 | 195 | 11.1 | |
| | | 4.7 | 18.58 | 20.3 | 19.1 | 192 | 10.0 | |
| | | 6.1 | 19.55 | 20.4 | | | | |
| 3 | 433 | 0 | 1.42 | 12.88 | 37.2 | 337 | 10.6 | |
| | | 1.1 | 4.29 | 12.4 | 35.3 | 320 | 11.7 | |
| | | 3.2 | 8.35 | 12.4 | 33.6 | 305 | 15.7 | |
| | | 4.3 | 10.01 | 12.55 | | | | |
| 4 | 416 | 0 | 10.06 | 12.55 | 33.6 | 275 | 10.8 | After run 3 |
| | | 0.9 | 10.65 | 12.55 | 31.9 | 274 | 8.08 | |
| | | 2.4 | 11.25 | 12.55 | | | | |
| 5 | 433 | 0 | 1.89 | 33.95 | 11.1 | 102 | 7.0 | |
| | | 0.63 | 12.02 | 33.90 | | | | |
| 6 | 393 | 0 | 12.02 | 33.90 | 10.56 | 95.4 | 2.39 | After run 5 |
| | | 1.05 | 16.65 | 33.90 | 10.10 | 83.2 | 1.44 | |
| | | 2.90 | 20.7 | 34.1 | | | | |
| 7 | 351[a] | 0 | 21.4 | 34.1 | 9.2 | 74.3 | 0.30 | After run 6 |
| | | 0.9 | 21.9 | 34.1 | | | | |
| 8 | 351 | 0 | 21.9 | 34.1 | 8.9 | 74.3 | 1.78 | After run 7, 6.7 ml STP of hydrogen was added to the system |
| | | 0.83 | 23.9 | 34.1 | 8.5 | | 1.82 | |
| | | 1.20 | 24.5 | 34.1 | | | | |

[a] After run 6, the temperature of the catalyst was decreased to 351°C: after 5 min, the temperature was decreased to 360° and was then gradually decreased to 351°C within 15 min. The initial point of run 7 started 1.8 hr after the end of run 6. The value of $Z^N$ was changed from 20.7 to 21.4% during this period. From these values, the rate $V$ was estimated to be 0.31 ml STP/hr, which is close to the rate obtained at 351°C.

effect of hydrogen upon the rate of the reaction over a doubly-promoted iron synthetic ammonia catalyst which was carefully reduced as shown in our previous works (*7*, *8*).

## EXPERIMENTS

The catalyst used was a doubly-promoted iron synthetic ammonia catalyst (4.72% alumina, 0.31% potassium oxide, and 0.05% silica as promoters) which was a different portion of the same preparation as that used in previous experiments of ammonia decomposition (*8*).

Two series of experiments were carried out in the circulating system with 2.16 g of the catalyst (before reduction) with granules from 12–14 mesh size. Series I and II experiments were carried out on the catalyst reduced in a stream of hydrogen at a flow rate of 500 ml STP/min at 450°C for 50 hr and, further, at 600°C for 50 hr.

Between the runs in the series, the catalyst was reduced overnight and degassed for 2 hr to $10^{-6}$ mm Hg at the respective reduction temperatures, unless otherwise stated in the tables.

The hydrogen was carefully purified by passing it through a palladium–silver alloy thimble and a trap immersed in liquid nitrogen. Thereby it was ensured that the hydrogen used was free from nitrogen and oxygen.

Ordinary nitrogen in a cylinder was purified by passing it through reduced nickel turnings (500°C), reduced copper gauze (500°C), silica gel, and then through reduced iron synthetic ammonia catalyst (500°C), and finally through a trap immersed in liquid nitrogen. Heavy nitrogen (95.1% $^{15}N$ atomic fraction) in its pure form (purchased from Isomet Corp., N. J.) was used without further purification.

The gas used for the reaction was prepared by mixing the ordinary nitrogen with the heavy nitrogen. The isotope composition of gas mixture was determined by Hitachi-RMU mass spectrometer after a small amount of gas was withdrawn from the system for analysis.

While the effect of hydrogen upon the reaction was being studied, the sampled gas was initially brought into contact with a molecular sieve 5A kept at −195°C and degassed at the same temperature in order to remove hydrogen, since it strongly affects the mass spectroscopic analysis for the isotope composition of nitrogen (*9*).

The surface area, the promoter distribution and the proportion of the surface covered with iron were estimated from the separate experiments by the conventional methods of Brunauer *et al.* (*10*) and Brunauer and Emmett (*11*). Those values are shown in Tables 1 and 2 for series I and II of the experiments, respectively.

## RESULTS AND DISCUSSION

### *Rate of the Exchange Reaction*

The results are listed in Tables 1 and 2 for the respective series I and II of experiments. In Tables 1 and 2, $T$ represents the reaction temperature and $P$ the partial pressure of nitrogen; $V$, the rate of the desorption of nitrogen was estimated from the equation

$$V = -(A/t)\ln(Z_e^N - Z_0^N)/(Z_e^N - Z^N),$$

in which the assumption was made that all nitrogen desorbing from the surface is statistically in equilibrium with respect to three molecular forms $^{28}N_2$, $^{29}N_2$, and $^{30}N_2$. $Z^N$, $Z_0^N$, and $Z_e^N$ are mole fractions of $^{29}N_2$

TABLE 2

NITROGEN EQUILIBRATION REACTION $^{28}N_2 + {}^{30}N_2 = 2{}^{29}N_2$ OVER THE DOUBLY-PROMOTED IRON CATALYST REDUCED AT 600°C AFTER SERIES I EXPERIMENTS (Series II expts.)

Catalyst used, 2.6 g; surface area, 12.0 m²/g; proportion of the surface covered with iron, 18.0%; potassium oxide, 29.2%; alumina and/or silica, 52.8%.

| Run | Temp $T$ (°C) | Time $t$ (hr) | $^{29}N_2$ $Z^N$ (%) | $^{29}N_2(e)$ $Z_e^N$ (%) | Vol of nitrogen in gas phase (ml STP) | $P$ (mm Hg) | $V$ (ml STP/hr) | Remarks |
|---|---|---|---|---|---|---|---|---|
| 1 | 433 | 0 | 1.42 | 20.6 | 14.25 | 128.6 | 9.82 | |
| | | 1.8 | 15.4 | 21.36 | | | | |
| 2 | 408 | 0 | 15.4 | 21.36 | 13.40 | 128.6 | 6.27 | After run 1 |
| | | 1.5 | 18.18 | 21.18 | 12.70 | 120.0 | 4.16 | |
| | | 2.0 | 18.63 | 21.25 | | | | |
| 3 | 408 | 0 | 18.63 | 21.25 | 11.13 | 160 | 5.57 | After run 2, 6.64 ml STP of hydrogen was added to the system |
| | | 0.75 | 19.40 | 20.78 | | | | |

at time $t$, $t = 0$ and the value at the equilibrium, respectively; $A$ represents the volume of nitrogen in the gas phase. It changed in a single run, because we drew off samples of the gas for the analysis. The value of $Z_e^N$ fluctuated somewhat due to the experimental errors which occurred during mass spectroscopic analysis of isotopes.

Figure 1 shows the effect of the partial pressure of nitrogen upon the rate. From the runs at 433°C in the series I experiments, the rate was found to be proportional to one-half the power of the partial pressure of nitrogen.

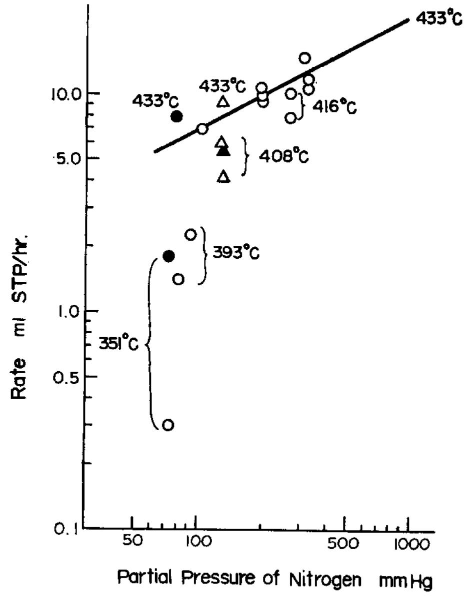

FIG. 1. The effect of the partial pressure of nitrogen upon the rates of equilibration reaction: (○) Series I experiments in the absence of hydrogen; (●) Series I experiments in the presence of hydrogen; (△) Series II experiment in the absence of hydrogen; (▲) Series II experiment in the presence of hydrogen.

The results in series I and II show that the rate $V$ was practically unchanged irrespective of the reduction temperatures. However, comparing the rate allotted to the surface area covered by iron, the rate in series II was about 1.5 times as fast as that in series I.

In Fig. 2 are shown the Arrhenius plots at the pressure of 100 mm Hg, assuming that the order of the reaction was one-half for all temperatures and pressures studied. The activation energy was thus estimated from the slope of the line in Fig. 1 at 33 kcal/mole for series I.

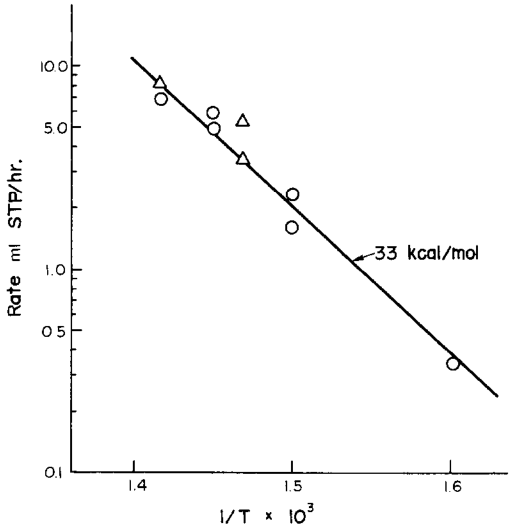

FIG. 2. Arrhenius plots of the equilibration reaction in the absence of hydrogen: (○) Series I experiments; (△) Series II experiment. The rates are estimated at the nitrogen pressure of 100 mm Hg assuming the order of the reaction is ½ at any temperatures.

One of the present authors and Emmett (*7*) recently studied the adsorptions of nitrogen and hydrogen over well-reduced iron synthetic ammonia catalysts. On the basis of their results, they pointed out that extremely pure hydrogen must be used for the reduction of the catalyst.

In view of the above fact, it is interesting to compare the present results with those of other workers. Joris and Taylor (*1*) studied the equilibration reaction, finding that the rate was extremely slow at 500°C. However, Kummer and Emmett (*2*) observed that the reaction proceeded at a considerable rate at 500°C when the catalyst was reduced carefully. The rate was thus obtained at 0.17 ml STP/hr g catalyst at a pressure of 60 mm Hg over the doubly-promoted iron catalyst (containing 0.8% alumina and 0.25% potassium oxide as promoters), whereas on the singly promoted iron catalysts (1.55% alumina and 0.58% zirconia) it amounted to 3.2 and 5.2 ml STP/hr g catalyst.

Boreskov and his co-workers (*4*, *5*) also studied the same reaction at temperatures ranging from 450 to 500°C.

These authors found that the reaction proceeded at a rate proportional to 0.5 to 0.6 the power of the partial pressure of nitrogen with the activation energy of 41.5 to 44 kcal/mole for the singly- and the doubly-promoted iron catalyst.* The rates obtained, on the other hand, were found to be in the range of $2.6 \times 10^{-2}$ to $2.6 \times 10^{-1}$ ml STP/hr $m^2$** at 500°C and at a pressure of 4.5 mm Hg.

It is, therefore, easily seen that the activation energy obtained in the present work was much lower than that obtained by Boreskov *et al.* (*4*, *5*), although the order of the reaction was practically the same.

For comparison of the rates, we should naturally consider those allotted to the surface area covered by iron because it is well known that the promoters partly cover the catalyst surface (*11*). However, no data were available for the proportion of the surface of the catalysts covered by iron in the other work (*4*, *5*). Furthermore, the present experimental conditions, such as the pressure or the temperatures, were somewhat different from those of other workers. Therefore, it is only possible to make qualitative comparisons of the rates if one assumes that (i) the order of the reaction and the activation energy were practically independent of the partial pressure of nitrogen and of the temperatures, and (ii) the proportion of the surface of their catalysts covered with iron was practically the same as that on the present catalyst. Thus extrapolating the rates obtained by Boreskov *et al.* (*4*, *5*) under the conditions at 400°C and the pressure of 100 mm Hg, the rate obtained in the present work was about 10 to 100 times as fast as that obtained by these authors.

As to the work by Kummer and Emmett (*2*), on the other hand, only the rate $V$ was available. Assuming that the surface area was the same as that of the present catalyst in addition to the assumptions (i) and (ii), the rate at 500°C on the singly- and the doubly-promoted catalysts used by them was roughly the same and one-hundredth of that of the present catalyst and 400°C, respectively.

It can be, therefore, shown that the present catalyst was much more active towards the equilibration reaction. This may be due to the reduction which was carried out by use of the hydrogen in a pure form.

In this connection, it should be interesting to compare the recent work of the nitrogen equilibration reaction over a well-reduced pure iron catalyst (*12*). With the present work the results on pure iron showed that the reaction proceeded at a rate proportional to one-half power of the partial pressure of nitrogen with the activation energy of 32 kcal/mole. The rate at 400°C, on the other hand, was estimated at 1.2 ml STP/hr $m^2$. These values are, in accord with the present results, in which the rate was estimated at 0.62 and 0.99 ml STP/hr $m^2$ of the iron surface in the respective series of I and II experiments.

### *Effect of Hydrogen upon the Exchange Reaction*

As mentioned in the introduction, it was found by other workers that the equilibration reaction was markedly accelerated in the presence of hydrogen above 450°C. As seen from the previous discussion, however, the experiments seem to have been carried out over a somewhat poorly reduced catalyst. The present experiments are, therefore, undertaken to examine whether or not such an effect is expected on a well-reduced catalyst.

Figure 1 and Tables 1 and 2 show that hydrogen practically exerted no influence upon the equilibration at 408 and 433°C; whereas at 351°C the rate of the reaction actually accelerated to a rate six times as fast as that recorded in the absence of hydrogen. Accordingly, these results are quite

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* Boreskov *et al.* (*4*, *5*) studied also the equilibration reaction over pure iron and the promoted iron containing only 2% of potassium oxide. These catalysts were also much less active compared to the present catalyst.

** Total surface area, not the surface area covered with iron.

different from those of the other workers.

Kazusaka and Toyoshima (*13*), recently studied the effect of hydrogen upon the rate of the equilibration reaction over various iron synthetic ammonia catalysts containing various amounts of potassium oxide covering from 0 to 1.54% with 2.5% alumina as promoters. The results clearly showed that the hydrogen effect was found on the singly-promoted catalyst, whereas no effect was found on the doubly-promoted catalyst. In this respect, the catalyst used in the present work seems to behave very much like a singly-promoted catalyst, because a much larger amount of alumina was contained in the present catalyst as compared with the amount of potassium oxide. The relative amount of alumina and potassium oxide in the catalyst must be the base of the discussion of the promoter function.

In this connection the authors recall the previous work done by Takezawa and Emmett (*7*) and Brunauer and Emmett (*14*) on the abnormal effect of adsorbed nitrogen upon the hydrogen adsorption on the singly-promoted catalyst. From the work, the conclusion was drawn that adsorbed imino or amino was existing predominantly on the singly-promoted catalysts as compared to that on the doubly-promoted catalyst.

The accelerating effect of hydrogen could be, therefore, attributed, in some part, to the formation of adsorbed imino or amino from hydrogen and adsorbed nitrogen.

In closing, the recent works by Takezawa (*15*) and Takezawa and Emmett (*16*) should be mentioned in which the presence of the different states of chemisorbed nitrogen was found on the well-reduced iron synthetic ammonia catalyst. From these results, it was suggested that nitrogen is predominantly held as molecular $\mathrm{N{\equiv}N{-}}$ or undissociative form $\mathrm{{=}N{-}N{=}}$ or $\mathrm{{-}N{=}N{-}}$ with lowering the temperature (near 200°C); whereas at higher temperatures (near 450°C) it is in a dissociative form $\mathrm{N{\equiv}}$. Therefore, nitrogen could be adsorbed predominantly in a dissociative form at 433 and 408°C. On the other hand, it could exist partially in an undissociative or molecular form at 351°C.

Admitting these results, the present results obtained at 351°C may be concerned with the occurrence of the hydrogenation of adsorbed nitrogen molecules or undissociatively adsorbed nitrogen with the formation of adsorbed imino NH or amino $NH_2$ by splitting the $\mathrm{N{\equiv}N}$, the $\mathrm{N{=}N}$, or the $\mathrm{N{-}N}$ bond.

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