Exchange Reaction between Deuterium and Ammonia on Synthetic Ammonia Catalysts Promoted Singly, Doubly, and Triply

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(Received May 22, 1956)

Introduction

A few investigations[1,2,3] have been made on the exchange reaction between deuterium and ammonia over iron catalysts for ammonia synthesis. Every one of them, however, confined the kinetic measurement to only one kind of the catalyst and no relation of the catalytic activity in the exchange reaction to the one in the ammonia synthesis is available as yet.

The present paper deals with the rate in the exchange reaction on three catalysts promoted by alumina with or without potash or potash and lime. The results presented here are of particular interest in connection with the catalyst performance in the ammonia synthesis.

Experimental Procedure

The rate of exchange reaction between deuterium and ammonia was determined on three kinds of fused iron catalysts, which was accompanied by the determinations of their surface area and the fractions of the surface covered by potash and of iron surface. The catalytic activity for ammonia synthesis was also evaluated.

Catalyst.—Catalysts for ammonia synthesis which were promoted singly, doubly, and triply respectively were employed in this investigation. Their promoter-compositions were (5% Al_2O_3), (5% Al_2O_3, 1% K_2O), and (4% Al_2O_3, 1% CaO, 1% K_2O). These catalysts were specimens taken from respective batches prepared for our previous investigations[4,5].

Catalytic Activity of Ammonia Synthesis.—The catalyst should exhaustively be reduced to be used for the determinations of the activity and of the rate of exchange reaction, and this was achieved as follows. A quantity (10 g.) of the catalyst granules rauging from 1 to 2 mm. in diameter was placed in a catalyst container (A in Fig. 1), and was reduced at 500°C in a current of a gas mixture composed of hydrogen and nitrogen in a ratio of 3: 1, which was passed over the catalyst at a space velocity of 2000. At various intervals in the reduction, the temperature was lowered to 350°C. and the exit gas from the container was quantitatively analyzed for ammonia. The reduction was continued until no more increase in the ammonia concentration was observed after six hours of further reduction. Usually about one hundred hours were required for the completion.

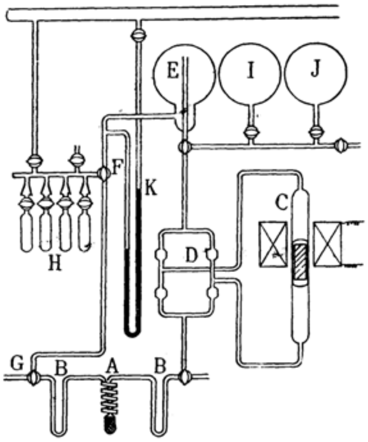

Fig. 1. Apparatus.

The ammonia concentration in the exit gas having passed over the catalyst at temperatures between 300° and 450°C at a space velocity of 2000 is employed as a measure of the activity of ammonia synthesis.

Rate of Exchange Reaction.—An apparatus similar to the one used by J. R. Gutmann[6] was employed for the determination of the rate. It is shown in Fig. 1. A catalyst container (A) is heated in an electric furnance and the catalyst is protected from contamination with the vapours of tap grease and mercury by U tubes (B, and B′) immersed in a melting chlorobenzene bath (−45°C). An all-glass electromagnetic pump (C, D) based on the design of J. Aman et al.[7] and having pumping capacity of 2.5 l/min. was used to prevent the effect of diffusion in gas phase on the rate. During the reaction, a part of the gas circulating successively through the container, a glass bulb (E, 1 l in volume), and the pump, was withdrawn by a three-way cock (F) into a small bottle (H), which was then removed from the apparatus and connected to another apparatus equipped with a thermo-conductivity gauge. The samples of the gas were freed from the included

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[1] H.S. Taylor and J.C. Jungers, *J. Am. Chem. Soc.*, **57**, 660 (1935).

[2] S. Enomoto, *Shokubai* (*Catalysis*), **8**, 47 (1952) (in Japanese).

[3] J. Weber and K.J. Laidler, *J. Chem. Phys.*, **19**, 1089 (1951).

[4] H. Uchida and M. Kuraishi, This Bulletin, **28**, 106 (1955).

[5] H. Uchida and N. Todo, ibid., **29**, 20 (1956).

[6] J.R. Gutmann, *J. Phys. Chem.*, **57**, 309 (1953).

[7] J. Aman, L. Farkas et al., *J. Am. Chem. Soc.*, **70**, 729 (1948).

ammonia by means of a liquid oxygen trap and then admitted into the gauge for the determination of the deuterium content. The gauge was kept at 0°C in a vigorously stirred mixture of ice and water, and the deuterium content could be determined to $\pm0.2\%$ at a pressure of 20 ± 0.05 mmHg adjusted by means of a leveling mercury reservoir and a cathetometer.

The deuterium was obtained by electrolysis from the heavy water supplied by Norsk Hydro-elektrisk Comp., by use of NaOD as electrolyte, and was purified by passing through a column of palladium asbestos and a liquid oxygen trap. A mixture of deuterium and hydrogen in a ratio of 1: 1 was used in the reaction. A mixing apparatus fitted with a manometer and a gas circulating pump was used to prepare the homogeneous mixture of deuterium and hydrogen, and mixture was then transferred into a reservoir (I) in Fig. 1, while ammonia was introduced into another one (J) after purification by drying over solid caustic potash and by fractional distillation in vacuo. From the reservoirs both the deuterium and the ammonia were introduced into the catalyst container to the desired composition by reading the pressures on a manometer (K).

The catalyst was degassed at 500°C till a high vacuum of 1×10^{-5} mmHg could be attained, and was then cooled down to the reaction temperature. After the admissions of the deuterium (50% D_2) and the ammonia, the circulating pump was started and the exchange reaction was followed by checking the deuterium content by analysis at definite time intervals.

Fractions of Surface Covered by Potash and of Iron Surface.—The fractions were determined according to the procedure by P. H. Emmett[8]. Nitrogen adsorption data were plotted according to the BET theory for obtaining the surface area, and the amount of carbon dioxide chemisorbed at −78°C was available for the determination of the fraction of the surface covered by potash, while the amount of carbon monoxide chemisorbed at −183°C was available for the determination of the fraction of the iron surface. In the latter case the amount at the pressure of 200 mmHg was employed for the determination, as the adsorbed amount remained constant independently of the increasing equilibrium pressure higher than this pressure[*1].

Results

Catalytic Activity for Ammonia Synthesis.—The results are shown in Fig. 2. The triply promoted catalyst revealed a higher activity than any other and was followed by the doubly promoted one. Their activities are of the same order as those at a high pressure of 100 kg./cm² (refer to our previous papers[4,5]).

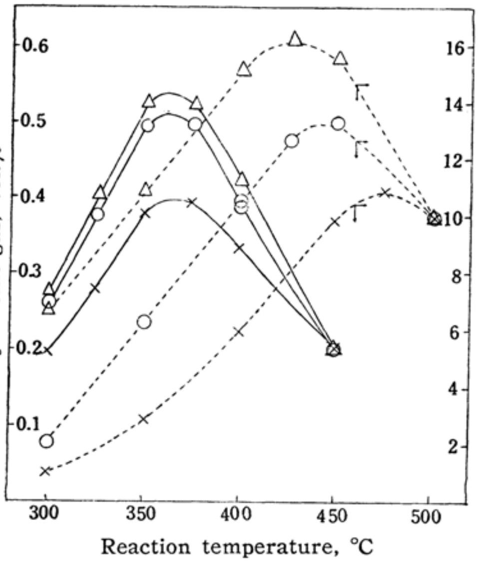

Fig. 2. Full line, results at a normal pressure at a S. V. of 2000: dotted line, results at 100 kg./cm² at a S. V. of 5000. ×, singly promoted catalyst, ○, doubly promoted catalyst, △, triply promoted catalyst.

Rate of Exchange Reaction.—The investigation was particularly concerned with establishing the relationship of the initial rate to the initial pressure of deuterium as well

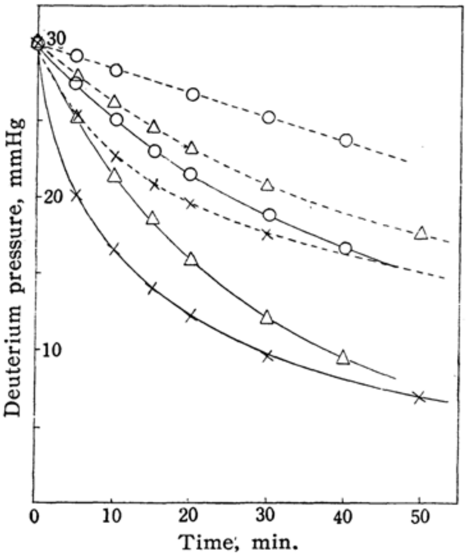

Fig. 3. Decrease in deuterium pressure with time.
Initial pressure of deuterium, 30 mmHg, initial pressure of ammonia, 120 mmHg. Full line, results at 150°C: dotted line, results at 130°C.
×, singly promoted catalyst: ○, doubly promoted catalyst: △, triply promoted catalyst.

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[8] P.H. Emmett, "Structure and Properties of Solid Surfaces" (edited by R. Gomer and C.S. Smith) (1952), p. 428.

[*1] The isotherm with the singly promoted catalyst, however, rose slightly with further increasing pressure.

as of ammonia. In this respect the measurement of the rate was carried out at a constant pressure of ammonia with varying pressures of deuterium and then at a constant pressure of deuterium with varying pressures of ammonia. The rates were measured at three different temperatures, 115°, 130°, and 150°C, on the three catalysts[*2].

In each kinetic run the deuterium pressure vs. time curve was determined. The results for a particular series are plotted in Fig. 3. From the figure the initial rate was obtained graphically by drawing the initial tangent. Fig. 4 presents the initial rate as a function of the square root of the initial deuterium pressure, at a constant ammonia pressure of 120 mmHg at 150°C. There is found a straight proportionality established between them, and the proportionality is also true with other series of runs at different temperatures.

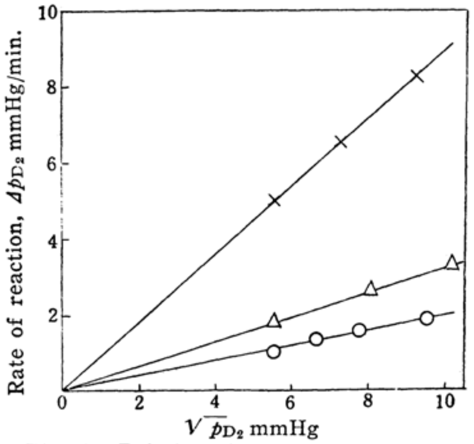
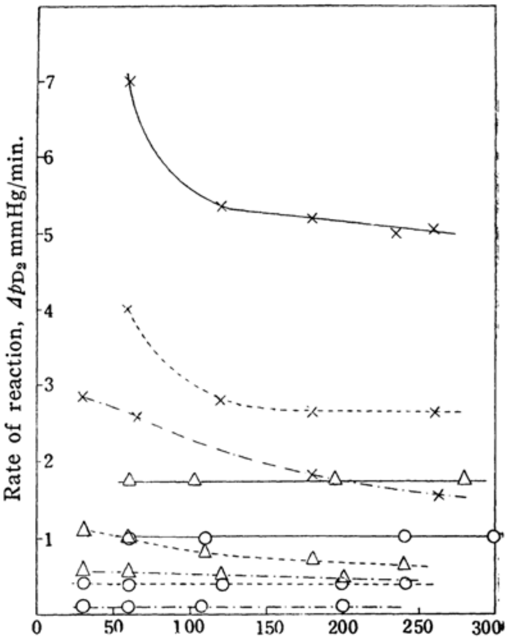


Fig. 4. Relation of reaction rate to square root of deuterium pressure.
Reaction temperature, 150°C, initial pressure of ammonia, 120 mmHg.
×, singly promoted catalyst: ○, doubly promoted catalyst: △, triply promoted catalyst.

The proportionality was found by A. Farkas[9] on an evaporated iron film, by J. Weber et al.[3] on a singly promoted iron catalyst, and also by J. Horiuti et al.[10] in the exchange reaction between nitrogen deuteride and hydrogen on nickel. On the other hand, J. R. Gutmann[6] and J. H. Singleton et al.[11] described the rate of first order with regard to deuterium pressure from their results obtained with the powders of iron and nickel and with an evaporated iron film respectively.

The rate was then determined at a constant pressure of deuterium (60 mmHg of 50% D_2), at 150°, 130°, and 115°C, with varying initial pressures of ammonia. The maximum and minimum ammonia pressures were 300 mm. and 30 mmHg respectively. The factors limiting the range of ammonia pressure were the vapour pressure of ammonia at −45°C, which was the temperature of U tubes (B, B′ in Fig. 1), and the accuracy of deuterium analysis in experiments where a high ratio of deuterium to ammonia resulted in too small a change of deuterium content for accurate determination.



Initial ammonia pressure, mmHg

Fig. 5. Dependence of initial rate upon initial ammonia pressure.
Full line, results at 150°C: dotted line, results at 130°C: dotted and dashed line, results at 115°C.
×, singly promoted catalyst: ○, doubly promoted catalyst: △, triply promoted catalyst.

The results are shown in Fig. 5 presenting the initial rate as a function of the initial ammonia pressure[*3]. The initial rates on the doubly promoted catalyst, at the three different temperatures, persisted unchanged independently of the varying initial pressures,

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[*2] Immediately after the reduction, the catalyst slightly decomposed the ammonia in the exchange reaction at 150°C. From run to run the decomposition tended to diminish in extent and simultaneously the rate became lower. After three or four runs there could hardly be recognized any decomposition of ammonia and the runs became reproducible in respect of the rate.

9) A. Farkas, *Trans. Faraday Soc.*, **32**, 416 (1936).
10) J. Horiuti and N. Suzuki, *Shokubai*, **4**, 1 (1948).
11) J.H. Singleton, E.R. Roberts and E.R.S. Winter, *Trans. Faraday Soc.*, **47**, 1318 (1951).

[*3] In the reaction with a low ammonia pressure of 30 mmHg, the rate at 115°C was too rapid to permit accurate measurement.

whereas the initial rate on the singly promoted one tended to decrease, at first, rapidly with the increasing initial ammonia pressure until it gradually approached a nearly constant value. At the high temperature of 150°C, the triply promoted catalyst was similar to the doubly promoted one in holding the initial rate constant; however, at the low temperatures of 130° and 115°C, it resembled the singly promoted one in revealing the decreasing rate with the increasing pressure of ammonia.

Our results observed with the doubly promoted catalyst are consistent with the rates observed by A. Farkas[9] on the evaporated iron film and by J. R. Gutmann[6] on the iron powder. Further, the kinetic results obtained by J. Weber et al.[3] with their singly promoted catalyst revealed a maximum of the rate at a certain ammonia pressure, from which the present results obtained with our singly promoted catalyst differed in giving the rate decreasing monotonously with the increasing initial ammonia pressure. The tendency found on the triply promoted catalyst coincides with the results obtained by J. H. Singleton et al.[11] on their evaporated iron film.

So far as the rate per 1 g. of catalyst is concerned, the rate is highest with the singly promoted catalyst, whereas it is lowest with the doubly promoted one.

Fractions of Surface Covered by Potash and of Iron Surface.—The results are listed in Table I. The catalysts have the surface area descending in the order of the triply promoted, singly promoted, and doubly promoted catalysts, while the fraction of the surface covered by potash decreases in the order of the doubly promoted, triply promoted, and singly promoted catalysts. The larger the fraction of the surface covered by potash, the smaller is that of iron.

TABLE I

SURFACE AREA AND FRACTIONS OF SURFACE COVERED BY POTASH AND OF IRON SURFACE

Catalyst	Surface Area m²/g. Oxide	Fraction of Surface Covered by Potash	Fraction of Iron Surface
Singly Promoted Catalyst	16.4	0.01	0.51
Doubly Promoted Catalyst	14.2	0.46	0.24
Triply Promoted Catalyst	18.4	0.28	0.44

Discussion

Rate of Exchange Reaction.—J. R. Gutmann[6] and J. H. Singleton et al.[11] represented their experimental rates by equation (1), while J. Horiuti et al.[10] expressed the rate by equation (2), both equations being based on the consideration of the rates of zeroth order with respect to the ammonia pressure. On the other hand J. Weber et al.[3] interpreted their results obtained with their singly promoted catalyst by equation (3), assuming the reaction to take place between an adsorbed deuterium atom and an adsorbed ammonia molecule. In the last equation the rate attains to a maximum value at a certain pressure of ammonia.

$$r = kp_{\mathrm{D_2}} \tag{1}$$

$$r = kp_{\mathrm{D_2}}^{1/2} \tag{2}$$

$$r = kp_{\mathrm{NH_3}}p_{\mathrm{D_2}}^{1/2}/(1+ap_{\mathrm{NH_3}}+bp_{\mathrm{D_2}}^{1/2})^2 \tag{3}$$

In our present investigation the initial rate was found to be proportional to the square root of the initial deuterium pressure but to depend differently upon the initial ammonia pressure according to the kind of the catalyst. The experimental rate may then be expressed by the following equation (4)

$$r = kp_{\mathrm{D_2}}^{1/2}/(1+ap_{\mathrm{NH_3}}+bp_{\mathrm{D_2}}^{1/2}) \tag{4}$$

The last term in the denominator may be ignored, since the relation observed between the initial rate and the square root of the initial deuterium pressure was linear. In the equation, a is an equilibrium adsorption constant of ammonia given by Langmuir's adsorption isotherm, and therefore takes different values according to the kind of the catalyst as well as the reaction temperature.

The equation suggests the rate to be based on the jump of dissociated deuterium atom from one site to another as the rate determining step, and to be retarded by the adsorption of ammonia on the surface more readily if the catalyst has the higher value of a.

Values of a may be predicted from the extent to which potash covers the surface, since the potash existing in the surface prevents the adsorption of ammonia. A larger value of a may thus reasonably be expected for the singly promoted catalyst whose surface is free from potash, whereas the extremely small one for the doubly promoted catalyst having the surface covered by potash to such an extent as a half of the total surface (refer to Table I), and this has appeared consistent qualitatively with the experimental rates for the singly promoted and doubly promoted catalysts. From the medium extent of the covering by potash found with the triply promoted catalyst, a value of a smaller than that for the singly promoted catalyst but larger than that for the doubly promoted one is expected for the catalyst. This can explain both the rate remaining constant independently of the increasing initial ammonia pressure at high temperatures where the value is comparatively small and the rate decreasing with the increasing initial pressure of ammonia at low temperatures where the value becomes larger.

TABLE III

RATES OF EXCHANGE REACTION AND AMMONIA SYNTHESIS BASED ON A DEFINITE SURFACE AREA OF IRON

Catalyst	Initial Rate of Exchange Reaction $(r/s\times\alpha)^*$, Δp_{D_2}/min.			Initial Rate of Ammonia Synthesis $(r'/s\times\alpha)^*$, Δp_{NH_3}/min., 350°C
	150°	130°	115°C	
Singly Promoted Catalyst	0.616	0.257	0.022	$0.61\cdot10^2$
Doubly Promoted Catalyst	0.293	0.073	0.027	$2.36\cdot10^2$
Triply Promoted Catalyst	0.216	0.070	0.027	$1.15\cdot10^2$

* In $r/s\times\alpha$, r is the rate of the exchange reaction, s is the surface area of the catalyst, and α is the fraction of iron surface. The initial rate of ammonia synthesis (r') at 350°C was calculated with the aid of Temkin's equation at the low pressure.

The apparent activation energies of the exchange reaction were obtained from Arrhenius plots of the rate constant k in equation (4), and are listed in Table II. The energy for the singly promoted catalyst is smaller than any other, and this probably contributes to the higher activity in the exchange reaction. Whereas the energies for the doubly promoted catalyst and the triply promoted one persist unchange independently of the varying pressures of ammonia, the energy for the singly promoted one tends to decrease with the increasing initial pressure of ammonia. The decrease was once found by J. Weber et al.[3] on their singly promoted catalyst and also by J. H. Singleton et al.[11] on the evaporated iron film. No certain explanation of the tendency can be available as yet.

TABLE II

APPARENT ACTIVATION ENERGY OF EXCHANGE REACTION

Catalyst	Apparent Activation Energy (kcal./mol.) at Initial Ammonia Pressure of		
	60	120	200 mmHg
Singly Promoted Catalyst	13.8	13.2	12.8
Doubly Promoted Catalyst	15.3	15.1	15.2
Triply Promoted Catalyst	14.2	14.1	14.1

Relation of Activity for Exchange Reaction to Activity for Ammonia Synthesis.—Considering that the exchange reaction as well as the synthesis takes place on the iron surface of the catalyst, both rates measured per an equal quantity of the catalyst are divided, for the sake of comparison, by the surface area multiplied by the fraction of the iron surface ($s\times\alpha$ in Table III). The results are shown in Table III[*4].

The rates thus obtained of the exchange reaction at 150° and 130°C for the singly promoted catalyst are remarkably higher than the rates for the others, of which the rate for the doubly promoted catalyst is slightly higher than that for the triply promoted one[*5]. The comparison of the rate in the exchange reaction with the one in the ammonia synthesis, both being based on a definite extent of iron surface (refer to Table II), reveals no parallel relation existing between them: the singly promoted catalyst of the highest rate in the exchange reaction gives the lowest rate in the ammonia synthesis, while the doubly promoted catalyst with the highest rate in the latter gives the markedly low rate in the former.

As described by H. S. Taylor[1], the rate involved in the equation (4) can not be expected to determine the rate of ammonia synthesis, since the exchange reaction will proceed with great rapidity at the high temperatures obtaining in the ammonia synthesis. Usually the rate in the ammonia synthesis is considered to be determined by the rate of activated adsorption of nitrogen. This, in connection with the results in the preceding paragraph, reveals the fact that the catalyst surface rapidly adsorbing deute-

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[*4] As for the singly promoted catalyst, the rate at the ammonia pressure of 200 mmHg was employed for the calculation. No remarkable decrease of the rate was observed beyond this ammonia pressure.

[*5] There has hardly ever been found any distinct difference between the activities for the exchange reaction at 115°C.

rium at the low temperatures slowly adsorbes nitrogen at the high temperatures. It, however, follows by no means that the surface is homogeneous, but it leads us to expect the surface as described by R. P. Eischens[12], which is rather heterogeneous, being divided into a few homogeneous portions. Either one of the portions will be predominant according to the promoter-composition.

Summary

The tendencies observed of the experimental rate (r) in the exchange reaction are represented by the following equation

$$r=kp_{D_2}^{1/2}/(1+ap_{NH_3}).$$

In the equation a is the equilibrium adsorption constant in Langmuir's isotherm. The value of a varies according to both the reaction temperature and the promoter-composition which causes different extents of the covering by potash on the surface after reduction.

The apparent activation energies in the exchange reaction are in a range of 15.3 to 12.8 kcal./mol. and the energy for the singly promoted catalyst is remakably smaller than the others. Whereas the energies for the doubly promoted and triply promoted catalysts persisted unchanged independently of the varying initial pressures of ammonia, the one for the singly promoted catalyst tended to decrease with the increasing initial pressure of ammonia.

The comparison of the rate in the exchange reaction with the one in ammonia synthesis, both being based on a definite extent of iron surface, reveals no parallel relation existing between them, namely the catalyst (the singly promoted catalyst) having the highest activity in the exchange reaction has a very low activity for the ammonia synthesis.

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[12] R. P. Eischens, *J. Am. Chem. Soc.*, **74**, 6167 (1952).