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Chemisorption of Gases on a Promoted Iron Catalyst

II. Exchange Between Deuterium and Preadsorbed Ammonia*

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As an extension of the study of chemisorption of gases on a promoted iron catalyst, the chemisorption of ammonia has been studied by the temperature-programmed desorption (TPD) and by the exchange reaction with deuterium. TPD generally gave three peaks, ammonia, hydrogen and nitrogen. When the amount of ammonia adsorbed was less than 9×10^{13} molecules/cm^2; however, all ammonia decomposed in TPD and gave only two peaks, hydrogen and nitrogen.

The exchange reaction between deuterium and ammonia preadsorbed on the surface was studied over a temperature range between −75 and 50°C. When ammonia was preadsorbed at room temperature, it was found that two distinctively different reactions took place: a fast exchange occurred at the initial stage to an extent that corresponded to the participation of one hydrogen atom of ammonia; and this fast reaction was followed by a slower exchange reaction which involved all hydrogen atoms of ammonia. The results suggest that ammonia adsorbed dissociates into amino radicals and hydrogen atoms on the surface, and upon the admission of deuterium the hydrogen atoms are quickly equilibrated with deuterium in the initial fast exchange reaction. The rate of transfer of hydrogen atoms from the gas phase to ammonia or vice versa was obtained from the slower exchange reaction, and some possible mechanisms were discussed.

INTRODUCTION

The exchange reaction between ammonia and deuterium on iron catalyst has been studied by several investigators since Taylor and Jungers reported that the reaction took place on a doubly promoted iron catalyst even at room temperature (*1*). Various types of catalyst were used: evaporated metal films (*2*–*4*), metal powders (*5*) and promoted iron catalysts for ammonia synthesis (*1*, *6*). The reaction was followed either by analyzing hydrogen or by analyzing ammonia. Thermal conductivity measurement was used for the former (*2*, *3*, *5*), while microwave absorption spectroscopy (*6*) or mass spectroscopy (*4*) was used for the latter. Although the reaction conditions used for the studies overlapped each other (10–500 Torr, 100–300°C), the kinetics has not yet been agreed upon completely. The reaction order was determined as the first order for deuterium by some investigators (*3*, *5*) but as 0.5th order by others (*2*, *6*), while most results showed that ammonia had no or slightly negative pressure dependence. Weber and Laidler reported that the rate showed a maximum with ammonia pressure (*6*).

The present work has been carried out as an extension of the preceding paper (*7*) of this series in order to obtain information on the chemisorption of ammonia on iron catalyst. There are two major differences in reaction conditions between the present work and those of previous workers. In the present experiments, most exchange reactions were carried out between deuterium gas and ammonia preadsorbed on a promoted iron catalyst instead of reacting the gaseous mixture of the two reactants. The reaction temperature was much lower

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(−75–50°C), so that no ammonia desorbed from the surface during reaction. Since there was no ammonia in the gas phase, the reaction was followed by analyzing the hydrogen isotopes gas chromatographically. The exchange reaction with the gaseous mixture of ammonia and deuterium was also carried out for comparison. The temperature-programmed desorption of ammonia was studied before the exchange reaction to obtain information on the strength of chemisorption.

EXPERIMENTAL METHODS

Materials

Following the study of chemisorption with hydrogen, nitrogen, carbon monoxide, and carbon dioxide which was reported in the preceding paper (*7*), the same sample of catalyst was used in the present study. It was 5.17 g of a Haldor Topsøe Type KM I iron catalyst promoted by K_2O, CaO, MgO, and Al_2O_3, kindly supplied by the Cominco Ltd., British Columbia, Canada, as reported previously.

Matheson's anhydrous ammonia was taken from a cylinder and degassed a couple of times by freezing at liquid nitrogen temperature before it was stored in a reservoir. C. P. grade deuterium also purchased from Matheson was passed through a spiral-type trap cooled by liquid nitrogen. HD at a concentration of 0.5% was the only impurity detected by gas chromatography. The purification of other gases was described previously (*7*).

Apparatus and Procedure

The apparatus and the treatment of the catalyst were also described in detail in the preceding paper (*7*). Ammonia was adsorbed before reaction, and the amount was so small in most experiments that there was no appreciable pressure remaining in the gas phase (less than 10^{-3} Torr). The reactor was isolated by means of a stopcock, and the rest of the reaction system was filled with deuterium, the amount of which was measured manometrically with a capacitance pressure transducer. The reaction was carried out by opening the stopcocks of the reactor and circulating deuterium through the reactor with a circulation pump which had been started beforehand. The pump was an all glass single-plunger type with polyethylene springs. The total volume of the reaction system was about 170 cc. In some experiments a trap located upstream of the reactor was cooled by liquid nitrogen to collect ammonia desorbed from the catalyst during the reaction. The amount collected in 110 min with the largest amount of ammonia preadsorbed in this study was found to be less than 3% of the preadsorbed amount showing that the desorption of ammonia was negligible.

A sample of gas was taken for analysis from time to time during the reaction (four samples in 110-min reaction) by expanding the gas phase into a small sampler. This procedure caused a decrease in the pressure each time by a few percent. The reaction rate was corrected for this pressure change as will be described later. The composition of hydrogen isotopes of the sample was determined by a gas chromatograph with a 2 *m* $MnCl_2$-impregnated alumina column at liquid nitrogen temperature according to the recipe of Yasumori and Ohno (*8*).

After each run, the catalyst was reduced in a flow of pure hydrogen at atmospheric pressure for a total of 2.5 hr. At the final stage of reduction, the temperature was increased to 700°C and the catalyst was evacuated for 30 min. The catalyst was reduced for more than 700 hr at 550°C in total before the present series of experiments were started. The catalyst was accidentally heated up to 900°C for a short period at the beginning of this study. After that, however, the activity remained stable and the surface area (3.93 m^2/g) measured by BET with nitrogen did not change within 2% during about thirty experiments required for the present paper.

Before the exchange reaction, the temperature-programmed desorption (TPD) of ammonia was carried out. TPD was described in detail in the previous paper (*7*).

RESULTS

I. Temperature-Programmed Desorption of Ammonia

A typical spectrum of TPD of ammonia is shown in Fig. 1. Ammonia was adsorbed at room temperature and at 1.8 Torr for 15 min. The pressure became constant in a couple of minutes, and ammonia weakly adsorbed was removed into a trap cooled by liquid nitrogen for 10 min before TPD. There was no detectable pressure during the removal of ammonia indicating that neither hydrogen nor nitrogen was formed in the gas phase by decomposition. The TPD was started from room temperature at a speed of about 20°C/min. Figure 1 was obtained by two experiments in which the adsorption was made under similar conditions but TPD was carried out in one with helium carrier gas, and in the other with argon carrier gas and a liquid nitrogen trap inserted between the reactor and the detector. Therefore, the former gave ammonia and nitrogen peaks while the latter gave only hydrogen peak at a moderate sensitivity used in these experiments. It should be noted, however, that the sensitivity of detecting gases in different carrier gases is not necessarily the same.

Figure 1 shows that ammonia molecules desorb at low temperatures (peak maximum at about 80°C) and those more strongly chemisorbed start decomposing at 100°C freeing hydrogen into the gas phase. As a result of decomposition, only nitrogen desorbs at high temperature. The temperature range over which nitrogen desorbs is the same as that obtained by adsorbing pure nitrogen as already pointed out in the previous paper (*7*). When larger amounts of ammonia were adsorbed either by lowering the adsorption temperature or by increasing the pressure, larger peaks of ammonia appeared, but they all finished at about 150°C similarly to Fig. 1 so that hydrogen peak was still well separated from that of undecomposed ammonia.

It is not clear at this stage whether undecomposed ammonia adsorbs on the promoter surface (alkalies–alumina) or on the metal surface. The adsorbed amount of ammonia exceeded the saturated amount of hydrogen already at 0.1 Torr, indicating that some ammonia certainly adsorbed on the promoter surface. Most of the adsorbed molecules, however, could be easily removed at room temperature by trapping into a liquid nitrogen trap for 10 min, and the amount of ammonia thus remaining on the surface (2.2×10^{14} molecules/cm^2) was less than the number of metal sites

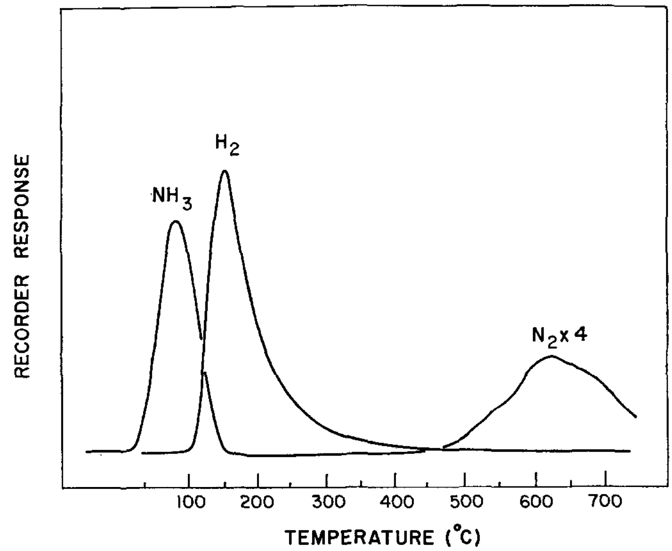

FIG. 1. TPD of ammonia.

(3.8×10^{14} sites/cm^2) estimated from the saturated amount of hydrogen (7). Also it is not very clear in Fig. 1 whether the decomposition is occurring competitively with the desorption of ammonia during heating or some ammonia adsorbs more strongly (dissociatively) than the other at the time of adsorption and goes to decomposition entirely at high temperature. If the former is the case, TPD spectrum usually gives an unresolved broad peak, so that the latter case is more likely as far as the TPD spectrum is concerned. When the adsorbed amount of ammonia was less than 9×10^{13} molecules/cm^2, no undecomposed ammonia peak appeared and the amount of hydrogen desorbed was 3/2 of adsorbed ammonia within an error of ±2%.

II. Exchange Reaction

1. H_2–D_2 exchange reaction. Hydrogen–deuterium exchange reaction was studied before the ammonia–deuterium exchange. Various amounts of hydrogen between 6.6×10^{13} and 1.4×10^{14} molecules/cm^2 were preadsorbed on the catalyst at -196, -75, 25, or 290°C. Deuterium was then circulated at a pressure of about 20 Torr through the catalyst, and the gas phase was analyzed from time to time (surface exchange reaction). No exchange occurred at -196°C at least up to 30 min. However, the exchange reaction became so fast at temperatures higher than -75° that the rate could not be measured. The composition of H_2, HD, and D_2 in the gas phase agreed within experimental error with the equilibrium composition calculated at the reaction temperatures by assuming that all hydrogen and deuterium in the system participated in the equilibrium. The equilibrium constant, K, used for the calculation was calculated by the equation $K = 4.24 \exp(-157/RT)$. In one experiment, an equimolar mixture of H_2 and D_2 was circulated at -75°C and at 20 Torr without preadsorption (equilibration reaction). Again the gas phase was quickly equilibrated (H_2:HD:D_2 = 28.0:45.5:26.5 found versus 27.0:45.8:27.1 calculated), in spite of the fact that 36% of the total gas remained adsorbed on the surface. It indicates that the atomic composition of hydrogen isotopes in the adsorbed phase is the same as that in the gas phase, in other words, there is no serious isotope effect on the adsorption at least at -75°C.

Finally, deuterium was circulated without preadsorption of hydrogen to see if any hydrogen left on the surface or in the bulk after treatment of catalyst carried out between runs as described in the "Experimental" section. The circulation was continued for 30 min at -75, 25, and 290°C, respectively, but no appreciable increase in H concentration was observed.

2. NH_3–D_2 exchange reaction. Some of the typical results of the exchange reaction are shown in Fig. 2 where the fraction of HD in the gas phase was plotted against reaction time. A constant amount of ammonia (9.0×10^{13} molecules/cm^2 or 1.8×10^{19} molecules in total) was preadsorbed at room temperature (about 25°C) for all reactions except for those shown by broken lines which will be explained later. As already described, this amount is the upper limit of preadsorbed ammonia all of which decomposed by TPD without desorbing undecomposed ammonia. It was also so small that there was no remaining pressure of ammonia in the gas phase. A constant amount of deuterium (2.9×10^{20} molecules) was then circulated through the catalyst at about 50 Torr and at various temperatures which were indicated under each curve in Fig. 2.

The equilibrium compositions of hydrogen isotopes in the gas phase were calculated by assuming that respectively one, two, and three hydrogen atoms of each ammonia molecule were equilibrated with deuterium admitted. It was also assumed that the atomic composition of the isotopes of adsorbed hydrogen was the same as that in the gas phase. This was confirmed in the case of H_2–D_2 exchange reaction as already described. The concentration of HD thus calculated was indicated in Fig. 2 by a shadowed band which was marked H, 2H, or 3H depending on the number of hydrogen atoms of ammonia involved in the equilibration. The width of the bands was

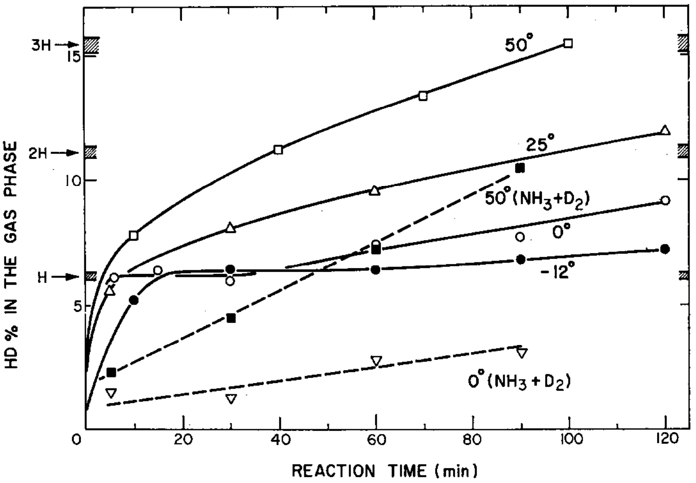

FIG. 2. D_2–NH_3 exchange reaction. Solid lines are the exchange between D_2 and NH_3 preadsorbed for about 90 min at 25°C before reaction. Broken lines are the exchange with the mixture of D_2 and NH_3. Reaction temperature is indicated under each curve, and the gas phase pressure was about 50 Torr for all experiments.

due to the fluctuation of the amounts of ammonia (±2%) and hydrogen (±1.5%). In the present experiments, the amount of deuterium was so large compared to the amount of hydrogen of ammonia that the calculated concentration of H_2 was less than 1%, and most H atoms existed as HD at all temperatures used even if all hydrogen atoms of ammonia participated in the reaction. Indeed H_2 actually found was negligible. Therefore, the exchange reaction can be followed simply by the concentration of HD in the gas phase which was plotted in Fig. 2.

A remarkable fact in Fig. 2 is that, at low temperatures (−12 and 0°C), the exchange reaction quickly produced about 6% of HD and almost stopped there for a while followed by a slow increase in HD concentration. This flat portion is at the H level which corresponds to the participation of one hydrogen atom of ammonia as already described. At room temperature or higher, the reaction did not stop and continued to higher concentration of HD as seen in Fig. 2. Nevertheless, it is clear that there is a distinct difference in the rate below and above the H level (about 6.2%) and that the reaction slowly but smoothly passes the 2H level (about 9.2%) at these high temperatures. The reaction reached the 3H level (about 15.5%) in 100 min at 50°C where all hydrogen atoms of ammonia were mixed with deuterium, but ammonia still remained adsorbed as already mentioned.

Two reactions were carried out at 0 and 50°C by circulating the mixture of ammonia and deuterium without preadsorption which were shown by broken lines in Fig. 2. The amounts of ammonia and deuterium were the same as those in the reactions already described. Although the measurement of adsorbed amount was not accurate in this large volume of the system, the pressure indicated that most of ammonia stayed adsorbed during the reaction. It is seen in Fig. 2 that the concentration of HD increases steadily without showing the rapid initial increase to the H level observed before. The reaction rate judged roughly from the slope of the curves are comparable with the slower portion of the reactions with preadsorbed ammonia at corresponding temperatures.

For the reactions described so far, ammonia was preadsorbed at 25°C, and the temperature of the catalyst was brought to the reaction temperature immediately before reaction. Thus, ammonia had been adsorbed at 25°C for approximately 90 min before the reaction was started. In one experiment, the adsorption time of ammonia at 25°C was shortened to 30 min followed by the exchange reaction at 25°C. The results were exactly the same as the 25°C curve in Fig. 2, so that the adsorption time did not affect the reaction at least after 30 min which was the shortest adsorption time feasible to arrange the measured amount of D_2 in the reaction system. On the other hand, the reaction was affected by the preadsorption temperature of ammonia as shown in Fig. 3, in which the preadsorption temperature and time were indicated on each curve. The results of Fig. 3 will be discussed again later.

After the experiments with the iron catalyst were finished, the catalyst was replaced by a sample (0.51 g) of pure alumina. The alumina was calcined in air for 4 hr at 600°C, and evacuated for 5 hr at the same temperature. Ammonia was then preadsorbed at room temperature and the temperature of the catalyst was increased up to 180°C in 1 hr where ammonia was trapped for 1 hr into a trap immersed in liquid nitrogen. The amount of ammonia thus remaining on the catalyst was 9.2×10^{13} molecules/cm² and deuterium was circulated at a pressure of about 50 Torr. No appreciable increase in HD over the impurity level was detected in 30 min at room temperature. The temperature was increased to 70°C for 30 min, and finally to 118°C for 30 min, but the increase in HD was found to be only 0.6% at 70°C and 1.5% at 118°C. The above results indicate that the possibility of exchange on either alumina or the wall of apparatus can be excluded at least at temperatures employed in the present study.

DISCUSSION

As already described in the preceding section, two kinds of exchange reaction between deuterium and preadsorbed ammonia take place at distinctively different rates under the reaction conditions used in the present study. The faster reaction which occurs at the initial stage will be discussed first. The fact that this exchange reaction proceeds quickly at low temperatures to an extent that corresponds to one hydrogen atom of ammonia, and that the surface exchange reaction between deuterium and preadsorbed hydrogen occurs very rapidly even at −75°C readily lead to a mechanism

$$1.\quad NH_3(a) \rightarrow NH_2(a) + H(a) \qquad (1a)$$

$$H(a) + D_2 \rightleftharpoons D(a) + HD. \qquad (1b)$$

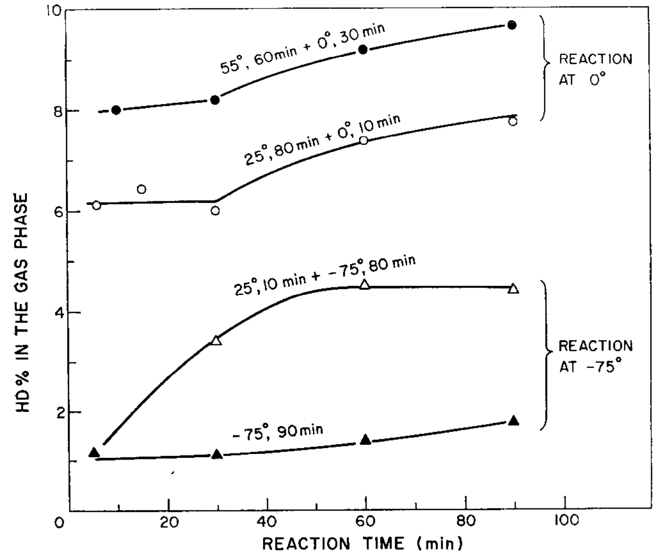

FIG. 3. Effect of preadsorption temperature of ammonia on the exchange reaction. The temperature and time of preadsorption are indicated on each curve. The pressure was about 50 Torr for all experiments.

When ammonia adsorbs on the iron surface, it dissociates almost completely at least at room temperature (1a), and hydrogen atoms thus produced are quickly mixed with deuterium (1b) which was observed at the initial stage of the reaction in Fig. 2. Any mechanism which involves a direct exchange between $NH_3(a)$ and deuterium including the formation of $NH_4(a)$ as intermediate cannot discriminate one hydrogen atom from the others in ammonia molecule. For the same reason, the exchange with amino or imino radical is excluded for the fast initial reaction. Although the dissociation of ammonia (1a) is almost complete at room temperature, the results of Fig. 3 indicate that very little dissociation occurred at −75°C, and 10 min adsorption at 25°C did not seem to be enough to dissociate completely. At 55°C, on the other hand, some ammonia would probably be dissociated further to imino radicals in 60 min.

When the mechanism of the slower exchange reaction is considered, it should be noted that the adsorption of deuterium (and HD formed) is in equilibrium or at least in quasi-equilibrium during the reaction except for the isotopic composition. The pressure of the gas phase did not change after a first minute or so, and no ammonia desorbed during the reaction as already mentioned. Some possible mechanisms for the slow exchange which involves all hydrogen atoms of ammonia are:

2. $NH_2(a) \rightarrow NH(a) + H(a)$ (2a)

$NH(a) \rightarrow N(a) + H(a)$ (2b)

3. $NH_2(a) + D(a) \rightleftharpoons NH_2D(a) + *$ (3)

4. $NH_2(a) + D_2 + * \rightleftharpoons NH_2D(a) + D(a)$ (4)

where the asterisk denotes a vacant site. Hydrogen atoms are released from ammonia by the dissociation of amino and imino radicals in Mechanism 2 or by the backward reactions of 3 and 4, and the released hydrogen is readily equilibrated with deuterium by the Reaction (1b) in all mechanisms.

If Mechanism 2 was the case, however, the Reactions (2a) and (2b) would have occurred as well as (1a) during the adsorption of ammonia. The 25°C curve in Fig. 2 shows that the exchange reaction beyond 6% of HD is slow at room temperature but it increases HD by about 5% in 90 min. As already mentioned, all curves in Fig. 2 were obtained by adsorbing ammonia for about 90 min at room temperature, so that they should have shown the fast initial exchange up to some 11% if mechanism 2 took place. It was also pointed out that the reaction with the mixture of D_2 and NH_3 (broken lines in Fig. 2) proceeded at roughly the same rate as the slower exchange with preadsorbed ammonia but lacked the fast exchange. It suggests that the former reaction takes place by the same mechanism under consideration, and Mechanism 2 cannot explain the lack of fast exchange.

Figure 4 shows the adsorption isotherm of deuterium at room temperature on the iron catalyst partially covered by ammonia. Two different amounts of ammonia were preadsorbed at room temperature and deuterium was then admitted for adsorption. Therefore, the conditions for experiments were similar to those for the exchange reaction, particularly in B where the amount of ammonia preadsorbed was approximately the same as that used for the reactions in Fig. 2. The adsorption was measured, however, in much smaller vol-

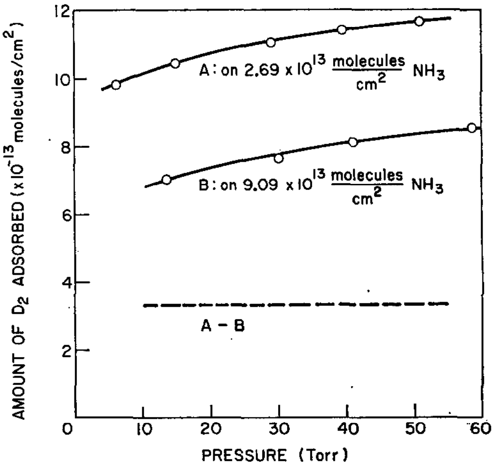

FIG. 4. Adsorption isotherm of deuterium at room temperature on ammonia-covered surface. The amount of ammonia preadsorbed is indicated in the figure.

ume (64 cc) and without circulation, so that the measurement of adsorption was much more accurate than in the reaction system. It is seen in Fig. 4 that the difference in adsorbed amount between A and B is quite constant (3.3×10^{13} molecules/cm^2) independent of pressure. The blocking factor of ammonia for deuterium was calculated as 0.52 by dividing (A–B) by the difference in preadsorbed ammonia. The value close to 0.5 indicates that one molecule of ammonia blocks one deuterium atom, while the blocking factor would become unity if ammonia remained dissociated as $NH_2 + H$ during reaction. Mechanisms 3 and 4 can give the blocking factor of approximately 0.5 if the equilibrium shifts to the right-hand side (molecular ammonia) as soon as deuterium is admitted. The reaction (1b) must be still faster particularly in Mechanism 3. Actually Mechanism 3 is the same as Mechanism 1 except for the recombination of $NH_2(a)$ and D(a) which may occur with a high concentration of deuterium atoms by the admission of deuterium in the gas phase. When a mixture of D_2 and NH_3 is reacted without preadsorption of ammonia, faster adsorption of deuterium will occupy the sites so that most ammonia adsorb as molecules from the beginning and only slow exchange takes place.

In order to simplify the following discussion, the word "hydrogen" will be used to include both protium and deuterium, and where necessary, the individual atoms will be designated as H and D. As already mentioned, there is no change in the amount of hydrogen in the gas phase, in the adsorbed phase or in ammonia molecules during the slow exchange reaction, while hydrogen atoms are transferred from the gas phase to ammonia molecules and vice versa. There is no rate-determining step in the sense that it is the slowest step between the elemental reactions involved. Instead the rate, v, is defined as the number of hydrogen atoms transferred from ammonia molecules to the gas phase in one second on 1 cm^2 of the surface, which should be equal to the rate of transfer in the reverse direction. Neglecting the isotope effect, the rate of increase in H atoms in the gas phase is expressed as

$$n(dx/dt) = Sv(x_a - x) \tag{5}$$

where n is the number of hydrogen atoms in the gas phase, S is the surface area (cm^2) of the catalyst, and x_a and x are the atomic fractions of H in ammonia molecules and in the gas phase, respectively. The total number of H atoms in the whole system, N_H, is constant and

$$x_a n_a + xn = N_H \tag{6}$$

where n_a is the number of hydrogen atoms in ammonia. Since the equilibration of hydrogen isotopes between the gas phase and adsorbed hydrogen is much faster, the number of hydrogen atoms adsorbed should be included in n whether the exchange takes place directly from the gas phase or through the adsorbed hydrogen.

From Eqs. (5) and (6), we have

$$ndx/dt = Sv[N_H/n_a - (n/n_a + 1)x].$$

Integrating above equation, the rate, v, is obtained as

$$v = \frac{nn_a}{St(n + n_a)} \ln \frac{N_H - (n + n_a)x_0}{N_H - (n + n_a)x}$$

where x_0 is the atomic fraction of H in the gas phase at $t = 0$. At equilibrium, $dx/dt = 0$ and therefore from (5) and (6),

$$x_a = x = x_\infty = N_H/N$$

where $N = n + n_a$, total number of hydrogen atoms in the system. Using this relation, v can be simplified as

$$v = (nn_a/StN) \ln(x_\infty - x_a)/(x_\infty - x). \tag{7}$$

The rate, v, was calculated by Eq. (7) for the slow exchange reactions carried out at 25°C by varying the deuterium pressure or preadsorbed amount of ammonia. The results are shown in Fig. 5. In these calculations, ammonia on the surface was assumed to be molecular (NH_3), and the rate was corrected for the decrease in hydrogen in the system caused by taking a small amount of sample for analysis. Figure 5 shows that the rate is approximately proportional to the hydrogen pressure and is retarded by ammonia. The Arrhenius plot

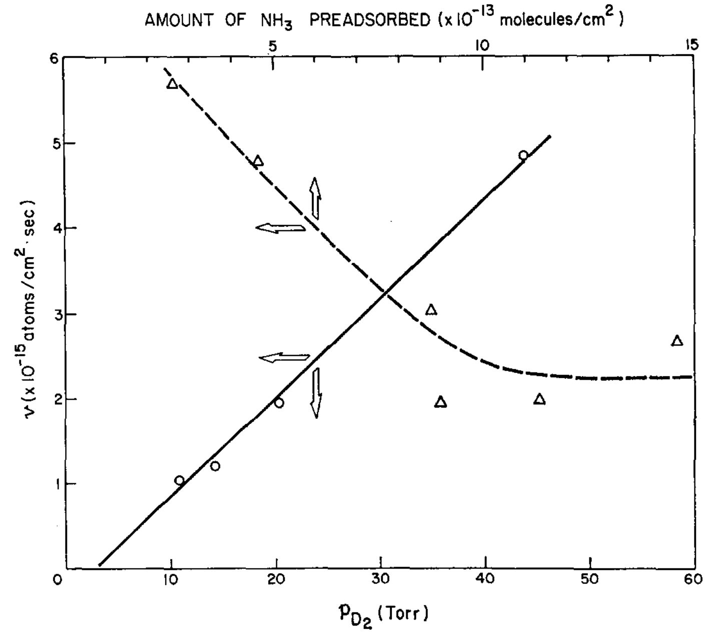

FIG. 5. Effects of deuterium and ammonia on the rate of slow exchange (v).

of v obtained from the reactions at different temperatures (Fig. 2) gave an activation energy of 6 kcal/mole. Since the adsorbed amount of hydrogen does not vary too much with the pressure as shown in Fig. 4, the first-order reaction for the hydrogen pressure favors Mechanism 4. However, the rate equations derived from 3 and 4 are complex functions of the surface concentrations of hydrogen and ammonia, so that more information is needed to determine the mechanism.

When the preadsorbed amount of ammonia was very large, the initial fast exchange did not reach the level corresponding to one hydrogen atom of ammonia. For example, the reaction with the largest amount of ammonia (1.46×10^{14} molecules/cm^2) shown in Fig. 5 gave 13% of HD in the initial fast exchange while the calculated H level was 19%. If this 13% is taken as the degree of dissociation as discussed, it shows that about 64% of ammonia on the surface dissociates into amino radicals and hydrogen atoms. Similar calculation also shows that all ammonia molecules dissociate when the surface concentration of ammonia is less than about 9×10^{13} molecules/cm^2 which agrees with the upper limit of ammonia decomposed completely during the temperature programmed desorption as already described.

In conclusion, it was found that there were two different modes of exchange reaction between deuterium and ammonia adsorbed on iron catalyst, although the mechanisms of exchange, particularly the slower exchange are still open to further studies.

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