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Ammonia Synthesis on Ruthenium Powder from 100 to 500°C and Hydrogenation of Preadsorbed Nitrogen down to −70°C

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The kinetic analysis of NH_3 synthesis over Ru shows that the rate law is $r = kP_{N_2} \cdot P_{H_2}^{-1} \cdot P^{\circ}_{NH_3}$ so that the reaction is limited by N_2 adsorption and inhibited by H_2. The limitation of rate by N_2 fixation is exemplified by the speed of hydrogenation of N_2 once it has been preadsorbed. Production of NH_3 has been observed down to −70°C. Hydrogenating the preadsorbed N_2 allows one to measure the extent of N_2 coverage and the rate of N_2 chemisorption on the bare surface. The latter gives the intrinsic catalytic activity of Ru which turns out to be from 500 to 2000 times higher than that of Fe corresponding to the temperature (400–250°C).

1. INTRODUCTION

We have previously reported the reason why we have been led to state that the synthesis of NH_3 displays an autocatalytic character on iron (*1–4*). Such a statement constitutes a very sure clue to forecast every transient of the catalyst which is unavoidably caused by the sudden change of any kinetic parameter of the reaction (*1, 2*) occurring under atmospheric pressure from about 200 to 500°C.

In order to know if such a conclusion could be extended to other metals, we have examined ruthenium, as it has already been recognized as a good catalyst for this reaction (*5–9*). We have observed no transient on that metal in its massive form so that the preceding statement cannot be applied to it. Commenting upon that situation would now remain a simple matter of speculation. Nevertheless, other very interesting kinetic features have appeared along the way, since that catalyst, usually studied at more than 300°C, turned out to be able to adsorb N_2 down to room temperature and to allow preadsorbed N_2 to react with H_2 down to nearly dry-ice temperature. The aim of the present article is to describe these results. Few comparisons can be made with previous studies, as most of them (*5–9*) deal with catalysts usually supported and promoted, mainly with potassium. Furthermore, previous work has mainly been concerned with reacting conditions corresponding to a narrow range of composition around the stoichiometric mixture and to temperatures usually higher than those of the present contribution.

2. EXPERIMENTAL

2.1. *Kinetic Measurements*

The experiments have been performed in a flow-type apparatus which has already been described (*1*) and which is operating still at atmospheric pressure.

The reactor may be fed with N_2, H_2, He, or any mixture of those gases after purification through Cu filings at 250°C and a trap filled with glass beads at liquid air temperature. The remaining O_2 content of the gases is lower than 0.05 ppm as estimated by a sensitive O_2 analyzer (Engelhard Mark II electrochemical meter). Except for the reactor, the whole apparatus is made of stainless steel pipes with *Swagelock* fittings and metallic valves. The flows of gases are held constant by Brooks flow controllers. They are measured by using a

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soap-bubble flowmeter at the exit of the apparatus.

The reactor is made of a tube of quartz and is equipped with a disk of fritted silica which supports the powder of Ru. The height and diameter of the catalyst bed are 1 mm and 2 cm, respectively. The volume of reactor flushed by the gases before contacting the catalyst is 75 cm^3 and is sufficient for their preheating. (The contact time is 6 s at a flow rate of 750 cm^3/min). The catalyst temperature is measured by means of a thermocouple situated in a well projecting into the bed.

The ammonia produced is determined by bubbling the reactor effluent through a sample of sulphuric acid solution (5 to 50 cm^3; 10^{-2}, 10^{-3}, or 10^{-4} N) and measuring the time which is required to neutralize the solution. The neutralization of the solution is continuously detected by means of a conductimetric cell. The steady rate of NH_3 production can thus be known within ±1% down to 10^{-8} mole · min^{-1}. Measuring so small a rate would require nearly 20 h in the closed circulating system frequently used (*5–9*).

Transient productions of NH_3 can also be measured easily by monitoring the progressive neutralization of a large enough volume of acid solution. The amount of acid neutralized is then derived from the variation of the conductivity. The quantity of N_2 adsorbed on Ru during an exposure of the metal to that gas can be measured also by substituting H_2 for N_2 and measuring the resulting amount of NH_3 according to the method just described.

As will be reported below, gases are frequently substituted for one another in the course of the present work. The time which is needed to clear the reactor is 6 s at the usual flow rate of 750 cm^3 · min^{-1}. However, the time which is meaningful on kinetic grounds is that which is required to clear the catalyst bed only; the latter is lower than 5×10^{-2} s so that gas substitutions may be regarded as instantaneous. Nevertheless, to make sure that there is no NH_3 produced due to the mixing of N_2 and H_2 by gaseous diffusion, both gases are separated by a short flow of He.

2.2. Catalyst

The catalyst is 1 g of Ru powder (Johnson Matthey Specpure Ru sponge, 30 ppm total impurity). Its active area (0.1 m^2 g^{-1}) can be determined as reported later by measuring the total amount of NH_3 which is produced under H_2 after it has been completely covered with N_2.

The powder is reduced under a flow of reactant mixture (N_2 + $3H_2$) while its temperature is increased progressively to 500°C.

The powder has been examined by means of an Auger electron spectrometer. The experimental arrangement consists of a Leybold-Heraeus spectrometer equipped with a preparation chamber which may be fed with gases at atmospheric pressure. The sample may be quickly transferred from it into the analysis chamber while being maintained under vacuum. The Auger spectrum does not allow one to detect any impurity other than oxygen which was chemisorbed onto the metal at room temperature before removing the sample from the reactor in order to prevent any other contamination during the transfer.

3. RESULTS

Once the reduction has been achieved the steady rate is almost immediately reached and remains very stable whenever any kinetic parameter is varied (temperature, mixture composition, flow rate). No reason therefore appears to assume any modification in the ruthenium surface under the reaction conditions.

3.1. Main Kinetic Features of the Reaction

There has been some recent controversy in the literature (*10*) concerning the influence of the flow rate (and therefore the ammonia pressure) upon the rate of reaction over dispersed Ru. That the reaction rate does not depend on the flow rate over Ru powder is well illustrated by the straight line 1 of Fig. 1 established at 308°C for a nearly stoichiometric mixture. It follows that the reaction has a zero order with respect to NH_3.

The straight line 2 (Fig. 1) shows that the reaction rate is exactly proportional to N_2 pressure between 0.05 and 0.27 atm, at 308°C.

Determining the order of reaction with respect to H_2 is a little more complicated as the lowering of H_2 pressure makes the rate increase, whereas the equilibrium value of NH_3 pressure decreases. The extent of reaction with respect to its equilibrium then exceeds 10% at 308°C. The result is that the back-reaction can no longer be neglected (*4*) and the rate of NH_3 production depends now on the flow rate. Decreasing the temperature to 280°C becomes necessary when the pressure of H_2 is decreased to 0.17 atm to reestablish a constant rate with respect to the flow rate (straight line 3). The variation of H_2 pressure from 0.17 to 0.73 atm at 280°C allows one to plot the straight line 4, which shows that the reaction rate is inversely proportional to P_{H_2} and thus strongly inhibited by H_2.

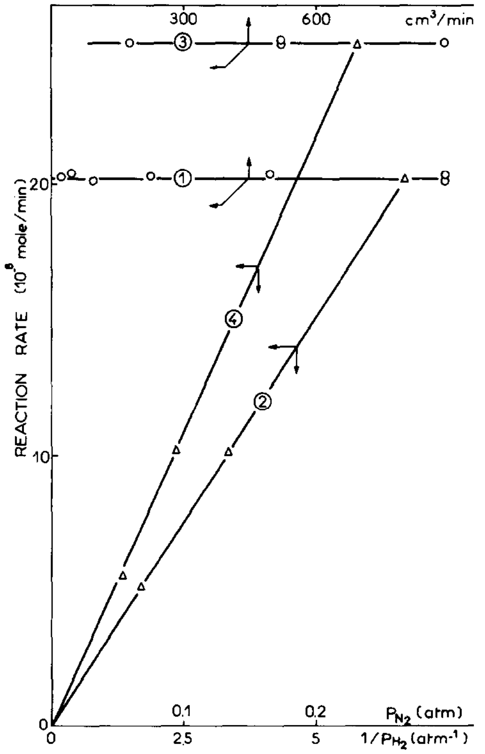

FIG. 1. (1) Reaction rate as a function of flow rate (27% N_2–73% H_2; 308°C). (2) Reaction rate as a function of N_2 pressure (P_{H_2} = 0.73 atm; 308°C). (3) Reaction rate as a function of flow rate (26% N_2–17% H_2; 57% He; 280°C). (4) Reaction rate as a function of $1/P_{H_2}$ (P_{N_2} = 0.26 atm; 280°C).

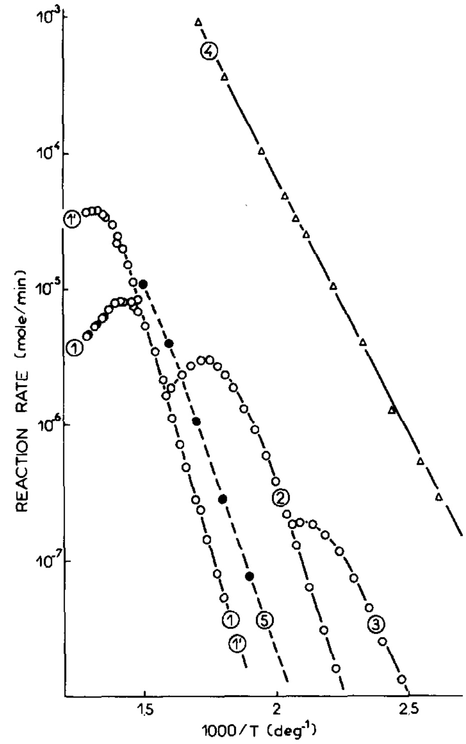

FIG. 2. Reaction rate as a function of $1/T$. (1) 100 cm³/min; 27% N_2–73% H_2. (1') 1000 cm³/min; 27% N_2–73% H_2. (2) 1000 cm³/min; 73% N_2–1.3% H_2–He. (3) 1000 cm³/min; 99% N_2–0.065% H_2–He. (4) Rate of adsorption of N_2 (0.27 atm) at zero coverage of the surface. (5) Reaction rate over 1 g of iron powder (same specific area as Ru) at zero extent of reaction (27% N_2–73% H_2).

The variation of the rate of reaction as a function of temperature is reported in Fig. 2. Curves 1 and 1′ refer to flow rates of 100 cm³/min and 1000 cm³/min of the nearly stoichiometric mixture. From the complete coincidence of the kinetic parts of those curves one can confirm that the rate of reaction does not depend on the flow rate except for the equilibrium region when the back reaction can no longer be neglected. No inhibition by NH_3 can therefore be observed, in sharp contrast to the case of iron. Corresponding to that mixture composition the limit of detection of the reaction is about 250°C.

As H_2 inhibits the reaction, a lower limit of detection is expected from a decrease of P_{H_2}. This can be observed on curves 2 (1.3×10^{-2} atm) and 3 (6.5×10^{-4} atm) for which the reaction rates become measurable at temperatures as low as 175 and 125°C. At higher temperatures the improvement of the catalyst activity does not result in production rates as high as might have been expected due to the fact that the decrease of H_2 pressure causes the equilibrium to shift toward lower NH_3 pressures.

It is worth noticing that decreasing the H_2 content down to 650 ppm does not suffice to make the inhibition disappear and a further improvement could still be reached. Nevertheless the range of temperatures within which the back reaction would remain negligible would be small.

Two preliminary conclusions emerge from these results, namely, the rate limitation of the reaction by N_2 adsorption (first order with respect to N_2) and the strong inhibition due to H_2. It is therefore in order to look for the behavior of Ru in the absence of these two limiting factors. We are thus led to adsorb pure N_2 on the bare surface of Ru to appreciate the extent of the inhibition by H_2. Let us notice that the initial rate of N_2 adsorption on the bare surface would equal the synthesis rate if no inhibition occurred due to H_2, as N_2 chemisorption constitutes the slow step. A second attempt should concern the direct revealing of the equilibrium which is expected to hold between chemisorbed N_2 and gaseous H_2 and NH_3.

3.2. *Adsorption of N_2 in the Absence of H_2*

In this new set of experiments the catalyst is exposed first to a flush of pure N_2 and then to a flush of pure H_2. The flow rate of each gas is high enough (750 cm^3/min.) for the catalyst bed to be cleared very quickly from the preceding feed ($<5.10^{-2}$ s). As already stated, the two gases are nevertheless separated by a short flow of He.

Curve 1 of Fig. 3 shows how the amount of N_2 adsorbed on the surface at 180°C increases as a function of the exposure length. Unexpectedly the rate of N_2 adsorption is zero initially and then increases until a maximum value is attained. One might have expected a maximum value at the beginning and a decrease thereafter as the surface coverage rose. The simplest way of explaining this delayed maximum is to assume that the surface is saturated initially with H_2 when it was exposed to N_2 and that some time is required for it to desorb under the N_2 exposure.

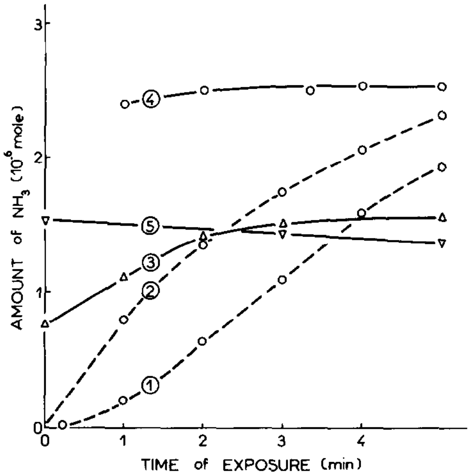

FIG. 3. Amounts of NH_3 resulting from hydrogenation of preadsorbed N_2 as a function of the length of the following flushes: (1) flush by pure N_2 (at 160°C) of the surface previously saturated with H_2. (2) Flush by pure N_2 (at 160°C) of the surface dehydrogenated under a flush of He (5 min). (3) Flush by pure He at 210°C. The catalyst had first been saturated with H_2 and the dehydrogenating He flush is followed by a standard feed with N_2 (3 min; 10^{-2} atm). (4) Flush by pure N_2 (at 210°C) of the surface dehydrogenated under a flush of He (3 min). (5) Flush by pure He at 210°C. The catalyst had first been dehydrogenated and then fed with N_2 (3 min; 10^{-2} atm).

In order to check this assumption the catalyst is exposed to a flush of pure helium after having been submitted to H_2 and before being resubmitted to N_2. Curve 2 is obtained in this way after the desorption of H_2 has been allowed to occur for 5 min under He at 160°C. The variation of the rate of adsorption turns out to be restored as expected.

To know how long the desorption of H_2 must be allowed under He for a clean surface to be obtained, the catalyst is saturated first with H_2, then flushed with He for a given time and finally subjected to a standard N_2 exposure just before hydrogenation. Curve 3 shows the result of that procedure at 210°C. One can see that 3 min of desorption under He are sufficient to clear the metal surface. The same thing would occur almost instantaneously at 300°C whereas it would need about 10 min at 100°C.

The amount of N_2 adsorbed on the catalyst levels off when the time of exposure to N_2 is high enough: curve 4 (Fig. 3) shows that under N_2 at 1 atm. 1 min. is almost sufficient at 210°C but about 10 or 100 min would be required at 160 or 100°C. The maximum amount of N_2 adsorbed remains constant at 100 to 300°C and begins to decrease from that temperature only. One can then assume that the surface can reach complete coverage up to 300°C whereas N_2 desorption begins to appear further. The amount of NH_3 which is produced from the saturated surface gives the number of sites which can adsorb N_2 in a form able to react with H_2 and which may therefore be reasonably assumed to be the active sites under the permanent conditions of reaction. The number of sites estimated thus is $L = 2.5\ 10^{-6}$ mole of sites/g corresponding to an active area of approximately 0.1 m^2/g.

As high coverages of the ruthenium surface are quickly reached under 1 atm of N_2 a new set of experiments has been carried out under a N_2 pressure reduced by diluting N_2 with helium (usually 0.7% N_2 in He). The catalyst, dehydrogenated first by a flush of pure He, is then fed with a N_2–He mixture for a given time. The following hydrogenation by pure H_2 makes it possible to determine the amount of N_2 adsorbed and dividing the latter by 2.5×10^{-6} allows one to deduce the surface coverage, θ_N, which had been attained.

The quantity $\theta_N/(1 - \theta_N)$ has been determined in this way and is plotted against the time of exposure in Fig. 4. It will be shown in the discussion section that

$$\frac{\theta_N}{1 - \theta_N} = \frac{r_0}{L} t,$$

r_0 being the rate of N_2 adsorption at zero coverage under the corresponding pressure of N_2. This equation holds provided that N_2 desorption does not occur. If this assumption does not hold, the variation is not expected to be linear, but the initial slope of the curves will continue to give r_0, as the desorption cannot occur at zero coverage.

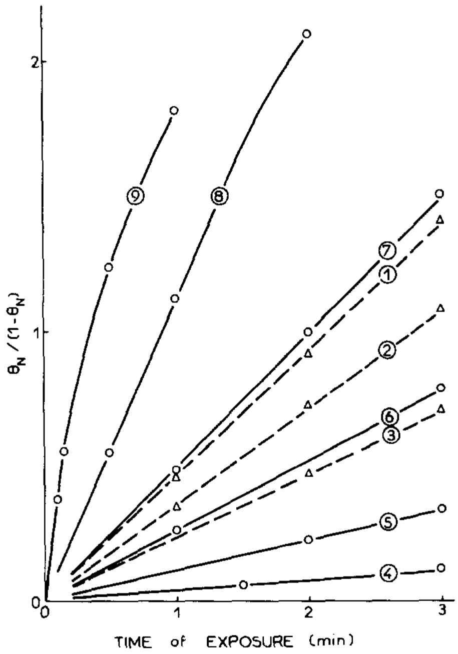

FIG. 4. $\theta_N/(1 - \theta_N)$ plotted against the length of flush by N_2 of the initially dehydrogenated catalyst. Influence of N_2 pressure at 210°C: (1) 10^{-2} atm; (2) 0.75×10^{-2} atm; (3) 0.5×10^{-2} atm. Influence of the temperature under 0.7 10^{-2} N_2: (4) 158°C; (5) 178°C; (6) 198°C; (7) 218°C; (8) 238°C; (9) 278°C.

Curves 1 to 7 show that straight lines are obtained up to 238°C in spite of the rather high coverages attained (up to 0.6). Curves 1, 2, and 3 relate to the same temperature (210°C) and make it possible to state that the rate of adsorption, r_0, is proportional to the pressure of N_2 (from 0.5 to 1.10^{-2} atm).

In order to estimate any possible (though small) influence of the desorption process in a better way, the catalyst is flushed with pure He for a given time, after a 3 min adsorption of N_2 under 10^{-2} atm (making $\theta_N = 0.6$) and just before the usual hydrogenation. Curve 5 (Fig. 3) illustrates the slowness of desorption at 210°C. At 100°C the surface remains completely saturated with N_2 even after a flush for 20 h of pure He. The spontaneous desorption of N_2 occurs however at higher temperatures since the plot of $\theta_N/1 - \theta_N$ starts curving in for a value of θ_N of about $\frac{1}{3}$ at 280°C. Our procedure could not be applied beyond 300°C because of the too fast desorption.

3.3. *Hydrogenation of Preadsorbed Nitrogen*

As already stated, we may expect the hydrogenation of preadsorbed N_2 to proceed at equilibrium under certain conditions. In order to show this it is appropriate to measure the rate of NH_3 produced from preadsorbed N_2 as a function of the flow rate of H_2, since the equilibrium should make the pressure of NH_3 constant at the reactor outlet. Furthermore, another way of displaying the high reactivity of preadsorbed N_2 is to show that it may react with H_2 at temperatures as low as possible.

Figure 5 illustrates the variation of the initial rate of hydrogenation as a function of the flow rate of H_2. The initial rate of hydrogenation is deduced from the rate at which the smallest volume (5 cm³) of acid solution (10^{-4} *N*) is first neutralized when H_2 is admitted upon the surface saturated with N_2. At temperatures lower than 100°C the adsorption of N_2 remains measurable down to room temperature but it becomes so slow that it is faster to saturate the catalyst with N_2 at 200°C first and then flush it with H_2 after cooling to the chosen temperature.

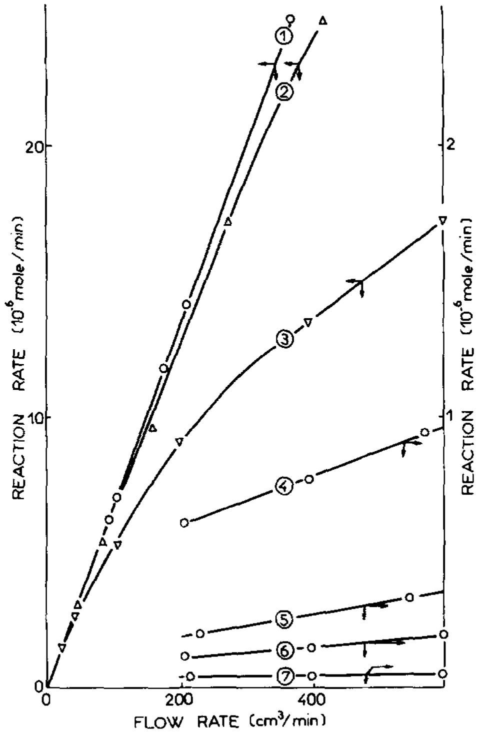

FIG. 5. Initial rate of hydrogenation of the surface initially saturated with N_2 as a function of the flow rate of pure H_2. (1) 256°C; (2) 158°C; (3) 80°C; (4) 13°C; (5) 2°C; (6) −6°C; (7) −23°C.

One can see that from 256°C (curve 1) to 158°C (curve 2) the initial rate of hydrogenation is proportional to the flow rate of H_2 and nearly independent of the temperature. It follows from the constancy of NH_3 pressure at the reactor outlet when the flow rate is varied that NH_3 is produced in equilibrium with the nitrogenated surface within that temperature range. At 80°C (curve 3) the equilibrium between chemisorbed N_2 and gaseous NH_3 operates still for low flow rates but progressively gives place to a reversible hydrogenation for higher flow rates. The influence of the flow rate diminishes little by little when the temperature of the experiment decreases, as can be seen on curves 4 (13°C), 5 (2°C), and 6 (−6°C); it becomes undiscernible on curve 7 (−23°C) and N_2 hydrogenation is irreversible at lower temperatures.

The hydrogenation can also be determined as a function of time instead of being measured merely at its start. The results are displayed in Fig. 6, where the total amount of NH_3 produced since the beginning of the hydrogenation is plotted against the time of reaction. A medium flow rate (600 cm^3/min.) has been chosen for these experiments and H_2 has been used either pure or diluted (5%) in helium. At 260°C (curve 1) most of the preadsorbed N_2 reacts almost immediately (80% in 5×10^{-2} min; 90% in 1 min). The hydrogenation starts more slowly under 0.05 atm of H_2 (curve 2) but becomes almost identical with the rate for 1 atm H_2 after 1 min. The influence of the flow rate is displayed only at the beginning as the variation of the amount of NH_3 becomes quickly identical with that depicted by the upper parts of curves 1 and 2. The rate is not much reduced at 80°C (curves 3 and 3′) but N_2 reacts with more difficulty at room temperature as can be seen in curves 4 ($P_{H_2} = 1$ atm) and 5 ($P_{H_2} = 0.05$ atm). Much more than 15 min would be required to extract the whole of the N_2 from the surface. The reaction is still observed easily at lower temperatures like −8°C (curve 6) or −35°C on curves 7 ($P_{H_2} = 1$ atm) and 8 ($P_{H_2} = 0.05$ atm.) and turns out to remain little influenced by the pressure of H_2. At −50°C the slackening of the reaction is sufficient to reveal a period of increasing rate (curve 9). This period lengthens at lower temperatures (curves 10 at −61°C and 11 at −71°C).

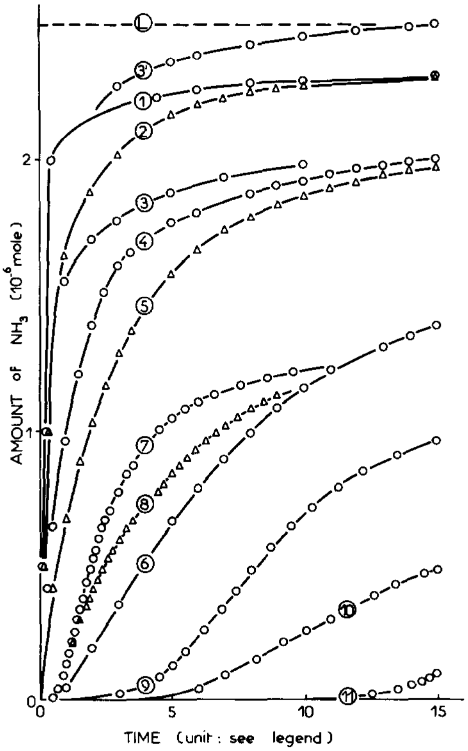

FIG. 6. Amounts of NH_3 resulting from hydrogenation of the surface initially saturated with N_2 as a function of time on stream under H_2. ($P_{H_2} = 1$ atm: ○; $P_{H_2} = 0.05$ atm: △). (1)–(3), time unit: 0.1 min; (1) and (2): 260°C; (3): 80°C. (3)–(6), time unit: 1 min; (3′): 80°C; (4) and (5): 27°C; (6): −8°C. (7)–(11), time unit: 10 min; (7) and (8): −35°C; (9): −50°C; (10): −61°C; (11): −71°C.

At −80°C NH_3 can no more be detected within 150 min but if the catalyst has been maintained at that temperature under H_2 for 150 min the period of increasing rate of curve 9 disappears when the catalyst is then heated to −50°C. Some partial hydrogenation must therefore occur on the surface even at as low a temperature as −80°C.

4. DISCUSSION

It is usually assumed (5) that, as for iron, the dissociative adsorption of N_2 on surface (S) atoms

$$S\text{-}S + N_2 \rightarrow 2SN \qquad (1)$$

is the slow step of NH_3 synthesis on Ru. We arrive at the same conclusion in the present work for two reasons. First the reaction rate is of order 1 with respect to N_2. The second reason relates obviously to the speed of reaction once N_2 has been preadsorbed even in a range of temperatures lying far below that usually explored in NH_3 synthesis. The remaining steps proceed therefore under equilibrium and can be expressed as a whole as follows:

$$SN + \tfrac{3}{2} H_2 = NH_3 + S. \qquad (2)$$

The coverage of the surface with nitrogenated species is therefore imposed by the equilibrium constants corresponding to the hydrogenation into NH_3 of the various possible intermediate species concurrently with that referring to the adsorption of H_2:

$$S{-}S + H_2 = 2SH \tag{3}$$

and with the pressure of H_2.

As in most of our experimental conditions the rate of reaction turns out to be unaffected by the variation of the flow rate, one can conclude that the coverages of the surface with nitrogenated species are very small. This is due to the high values of the equilibrium constants of hydrogenation into NH_3 of every nitrogenated species. It is in agreement with the fact that preadsorbed nitrogen is very quickly extracted from the surface. It may be stressed here that the situation is very different from that of iron upon which the influence of the flow rate is always present whereas a long time is needed to hydrogenate fully the preadsorbed N_2 (*3*).

The rate of the steady reaction (expressed as the molar amount of NH_3 produced per minute on 1 g of powder) is that of step (1):

$$r = 2k\,(S{-}S)\,P_{N_2},$$

where k is the rate constant of step (1) and $(S{-}S)$ stands for the number of different pairs of neighbor sites consisting of distinct and bare atoms of metal. Their maximum number being $L/2$ and the surface being covered mainly with hydrogen,

$$(S{-}S) = \frac{L}{2}(1 - \theta_H)^2.$$

Now

$$\theta_H = \frac{(SH)}{L} = \frac{(KP_{H_2})^{1/2}}{1 + (KP_{H_2})^{1/2}}, \tag{4}$$

where K is the equilibrium constant of Eq. (3).

It follows that the rate of reaction whenever the back reaction can be neglected is:

$$r = \frac{kLP_{N_2}}{[1 + (KP_{H_2})^{1/2}]^2} = \frac{r_0}{[1 + (KP_{H_2})^{1/2}]^2}, \tag{5}$$

where r_0 stands for the rate of adsorption of N_2 on the bare surface of 1 g of catalyst in the absence of H_2. In order to agree with the experimental −1 order with respect to H_2, it suffices to assume that the surface is nearly saturated with H_2, that is to say

$$(KP_{H_2})^{1/2} = \frac{(SH)}{(S)} \gg 1$$

so that

$$r = \frac{kLP_{N_2}}{KP_{H_2}} = \frac{r_0}{KP_{H_2}}. \tag{6}$$

As we have measured the amounts of N_2 adsorbed as a function of the time of exposure to N_2 we can reach r_0 directly. This is most conveniently done from the curves of Fig. 4. We can indeed state that when the clean surface has been exposed to N_2 for a time t:

$$\frac{d(SN)}{dt} = L\frac{d\theta_N}{dt} = 2k(S{-}S)P_{N_2} = kL(1 - \theta_N)^2 P_{N_2}$$

from which it follows that:

$$\frac{\theta_N}{1 - \theta_N} = kP_{N_2}t = \frac{r_0}{L}t.$$

The result is that the slopes of the curves of Fig. 4 give very easy access to r_0 under the corresponding pressure of N_2. If one now takes into account the first order of r_0 with respect to P_{N_2} (curves 1, 2, and 3 of Fig. 4) the rate of N_2 adsorption corresponding to P_{N_2} in any reactant mixture can quickly be calculated for various temperatures. Curve 4 of Fig. 2 shows the result of such calculations if P_{N_2} = 0.27 atm and makes the comparison with curve 1 straightforward. The activation energy of the adsorption of N_2 is now easily derived (curve 4, 17 kcal/mole) and allows one, by subtraction from the activation energy of the reaction (curve 1, 31 kcal/mole) to know the heat of adsorption of H_2 (14 kcal/mole).

On the other hand, we may derive from Eq. (5) that

$$[1 + (KP_{H_2})^{1/2}]^2 = r_0/r,$$

which gives the means of computing $(KP_{H_2})^{1/2}$ and thus θ_H (Eq. 4) relating to any steady conditions. Table 1 gives the values of θ_H corresponding to conditions used for the establishment of curves 1, 2 and 3 of Fig. 2. It can thus be shown quantitatively that the ruthenium surface remains largely covered with H_2 even for very little H_2 contents in the reactant mixture. This coverage of the surface of Ru by H_2 might have been reasonably expected from Dalla Betta's work (*11*), according to which more than 80% of the surface of a Ru powder was quickly covered under 0.35 atm of H_2 at 21°C.

The very strong inhibition exerted by H_2 upon ruthenium is the reason which prevents it from displaying its maximum catalytic activity, which would otherwise equal that given by curve 4 (Fig. 2) for a corresponding N_2 pressure and which is 3 or 4 orders of magnitude higher than the activity level of curve 1.

Two questions now merit consideration. The first one relates to the objection which is raised sometimes that most discussions of the mechanism of NH_3 synthesis overlook the possibility of a molecular adsorption of N_2. That point may appear to have but a minor interest inasmuch as the slow step of the reaction remains the fixation of N_2 on the surface whatever the kind of adsorption may be. Nevertheless, we possess enough experimental evidence to discard the possibility of a molecular adsorption of N_2.

Let us assume indeed that N_2 adsorbs in a molecular form on the Ru surface and that the slow step is the dissociation into the atomic form. The kinetic sequence would be:

$$S + N_2 = SN_2 \qquad \text{(equilibrium constant } K'\text{)}$$

$$SN_2 + S \rightarrow 2SN \qquad \text{(rate constant } k'\text{)}$$

$$SN + \tfrac{3}{2}H_2 = S + NH_3$$

As NH_3 does not inhibit the reaction, the only chemisorbed species which have to be considered are SN_2 and SH. The reaction rate can be expressed as:

$$r = k'L(1 - \theta_H - \theta_{N_2})\theta_{N_2}$$

or

$$r = \frac{k'K'LP_{N_2}}{[1 + (KP_{H_2})^{1/2} + K'P_{N_2}]^2}.$$

In order to explain the −1 order with respect to H_2, we may consider

$$(KP_{H_2})^{1/2} \gg 1 + K'P_{N_2}$$

so that

$$r = \frac{k'K'LP_{N_2}}{KP_{H_2}},$$

which is a rate law equivalent to Eq. (6) inasmuch as kinetic data of a steady character cannot discriminate between both equations. Other experimental evidence can be called upon nevertheless. If there were an equilibrated molecular adsorption of N_2,

TABLE 1

Hydrogen Coverages (θ_H) for Various Experimental Conditions in NH_3 Synthesis

Operating conditions	27% N_2, 73% H_2		73% N_2, 1.3% H_2		99% N_2, 0.065% H_2 125°C
	400°C	250°C	250°C	170°C	
θ_H	0.96	0.99	0.94	0.98	0.94

submitting the surface to a flow of pure He would bring about the desorption of N_2 and would not allow it to be reacted into NH_3. Just the reverse is observed and N_2 desorption cannot even be detected at low temperatures.

A different assumption might consist in a slow adsorption of molecular N_2:

$$S + N_2 \rightarrow SN_2 \qquad \text{(rate constant k'')},$$

followed by the overall quasi-equilibrium:

$$SN_2 + 3H_2 = S + 2NH_3.$$

Due to the absence of inhibition by NH_3 the only adsorbed species would be SH so that the rate law would be

$$r = \frac{2k''P_{N_2}L}{1 + (KP_{H_2})^{1/2}}$$

and the reaction order with respect to H_2 might not be explained.

The second question is concerned with our way of calculating θ_H. It relies upon the determination of r_0 and assumes therefore that every site of adsorption of N_2 is an active site in the steady conditions of reaction. Is there experimental evidence to support that assumption? We must notice first that a great advantage of the method used here to measure the rate of adsorption of N_2 is that the only sites which are accessible are those which chemisorbed N_2 *in a form able to give ammonia*. Moreover, we have shown that the equilibrium of Eq. (2) operates in the reactor effluent throughout the entire range of temperature used for the activity measurements in steady conditions. As the hydrogenation of N_2 preadsorbed is quickly completed, we must conclude that the equilibrium constant of Eq. (2) is *equally high* upon the whole chemisorbing area so that there is no experimental evidence for any heterogeneity of the *active* surface. It appears reasonable therefore to identify the area determined by our dynamic procedure with that responsible for the catalytic activity.

In order to compare the activities of Ru and Fe we have reported (curve 5, Fig. 2) that of 1 g of Fe powder (iron sponge, Specpure, Johnson & Matthey) of equal area (0.1 m^2) fed with the stoichiometric mixture as we have already determined it by using the same apparatus and procedures (*12*). The rate law upon Fe when the back reaction can be neglected is

$$r = \frac{r_0}{(1 + P_{NH_3}/K'P_{H_2}{}^{3/2})^2},$$

where r_0 has the same meaning as for Ru, and K' is the equilibrium constant of Eq. (2) for Fe. It is r_0 which is reported on curve 5 as it is free from inhibition by NH_3. It has been calculated from the variation of the rate of NH_3 production of the catalyst bed as a function of the exit pressure of NH_3 as previously reported for the case of a triply promoted industrial catalyst (KMI) (*4*). This rate therefore expresses the best, but virtual, catalytic activity of Fe under 0.27 atm of N_2 without it being necessary to mention H_2 pressure since that extrapolated rate is of order zero with respect to H_2. It therefore directly compares with r_0 for Ru corresponding to the same N_2 pressure (curve 4). The optimum activity of Fe appears somewhat higher than that of Ru as far as the latter is fed with the stoichiometric mixture. Nevertheless, the intrinsic activity of Ru can pas beyond that of Fe by more than one order of magnitude if the pressure of H_2 is depressed (rate r_0 over Fe unchanged) as can be seen in curves 2 and 3 of Fig. 2.

It remains to state that two reasons prevent one from taking as large an advantage as possible from the lowering of H_2 pressure over Ru. The first one is that the very cause of the activity improvement makes the equilibrium shift toward lower NH_3 pressures and that is obviously detrimental to the rate of NH_3 production. The second one consists of the fact that in spite of a high decrease of H_2 pressure in the reactant mixture the catalyst has not been cleared from the inhibition by H_2 so that most of its intrinsic activity (r_0) remains potential. If that potential activity could be attained the activity of Ru would be above that of Fe by a factor of 500 to 2000 according to the temperature (400 to 250°C). We shall later report on ways of taking more advantage of the high intrinsic activity of Ru (*12*).

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