

Catalytic Effect of Iron Wires on the Syntheses of Ammonia and Hydrazine in a Radio-Frequency Discharge¹

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The catalytic effect of iron wires on plasma syntheses of ammonia and hydrazine has been studied in the nitrogen-hydrogen plasma prepared using rf discharge at a pressure of 650 Pa (5 Torr). The product was mainly ammonia including a small amount of hydrazine. When iron wires were placed in the plasma downstream of the gas flow, the yields of both products increased, about two times in ammonia and two orders of magnitude in hydrazine. The yields increased with increasing number of wires (the surface area of the catalyst). The dissociative adsorption of nitrogen molecules and/or molecular ions on the iron surface and the formation of NH_x by the reaction with hydrogen in the plasma followed by the formation of NH_3 or N_2H_4 are considered as a reaction scheme. This is supported by the identification of NH_3 with XPS of the surface of iron wires.

KEY WORDS: Ammonia synthesis; hydrazine synthesis; Fe catalyst; rf discharge; plasma catalysis.

1. INTRODUCTION

The plasma synthesis of ammonia is a complex process and is influenced by surface and catalytic effects.⁽¹⁻³⁾ When an iron catalyst was used as electrode material and was placed in the plasma region or in the afterglow region of the nitrogen-hydrogen plasma prepared by dc or low frequency ac discharges, the ammonia yield was enhanced.⁽⁴⁾ The ammonia formation

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reactions may be catalyzed by the surface of iron.⁽¹⁾ The mechanisms of surface-catalyzed reactions must involve a sequence of steps:

1. adsorption of the reacting species on the surface,
2. reaction on the surface, and
3. desorption of the products.

On the iron surface in the nitrogen-hydrogen plasma, adsorbed nitrogen atoms formed by dissociative adsorption of excited nitrogen molecules⁽⁴⁾ or nitrogen molecular ions⁽⁵⁾ would react with hydrogen atoms or molecules formed in the plasma. Ammonia would be formed on the iron surface and then be desorbed. Moreover, hydrazine may be formed by the reaction between adsorbed ammonia and NH radicals formed in the plasma.^(1,5) Experimental evidences for the reaction schemes have not been proposed, except that some reactive species in the plasma were identified.^(1,4) Thus, it is necessary to offer other experimental evidence, especially those of the adsorbed species on the surface of catalyst.

On the other hand, we have studied the nitriding of iron in the plasma prepared using rf discharge⁽⁶⁾ and the interaction of nitrified iron with hydrogen plasma⁽⁷⁾ prepared in the same way as the nitrogen-hydrogen plasma. It was not known whether the nitriding of iron was responsible for high yields of ammonia as well as hydrazine.⁽¹⁾ Therefore, it is also necessary to clarify the role of nitride formation for the increase of ammonia and hydrazine yields in detail.

We have investigated the syntheses of ammonia as well as hydrazine in the nitrogen-hydrogen plasma prepared using rf discharge in the presence or absence of iron wires as the catalyst. As mentioned above, the surface analysis of the iron is needed in addition to the identification of reactive species in the plasma to investigate the catalytic effect of iron wires on ammonia as well as hydrazine syntheses. In the present paper, the catalytic effect of iron wires on the syntheses of ammonia and hydrazine in the nitrogen-hydrogen plasma prepared using rf discharge is discussed based on the surface analysis in addition to plasma diagnostics.

2. EXPERIMENTAL

2.1. Materials

Iron wires (99.99% purity, 0.5 mm in diameter, and 50 mm long) were bound in a desired number to change the iron surface area. Molecular sieve 13X (1/16 inch pellet) was used for adsorption of products.⁽⁸⁾ The dehydrated zeolite was used in the ammonia adsorption and the hydrated zeolite was used in the hydrazine adsorption.⁽⁹⁾ Purified nitrogen and hydrogen (both 99.999%) were used as the plasma gas.

2.2. Apparatus and Experimental Procedures

The experimental apparatus and procedures for the syntheses of ammonia as well as hydrazine were the same as described previously.⁽⁶⁾ Before applying the discharge, the discharge tube was evacuated and then nitrogen-hydrogen gas mixture (mixing ratio was 4:1) was introduced. The rf power ($f = 13.56$ MHz) was applied inductively and the nitrogen-hydrogen plasma was prepared. Discharge conditions were as follows: gas flow rate, $1.2 \text{ dm}^3 \text{ h}^{-1}$ (20 sccm); pressure, 650 Pa (5 Torr); rf power absorbed, 160 W. The discharge was continued for varying periods in the range between 0.5 and 3 h. Ammonia and hydrazine as products were collected by adsorption on molecular sieves placed downstream of the gas flow at 273 K.⁽⁸⁾ The adsorbed amounts of ammonia and hydrazine on the molecular sieve were determined by the Kjeldahl method and absorptiometry, respectively.⁽⁹⁾ The bundle of iron wires was placed 150 mm from the center of the inductive coil and was located between the coil and the adsorbent of products (Fig. 1 in Ref. 8). The discharge was carried out with or without the iron wires. During the discharge, the iron wires were covered with plasma. The number of wires was changed to examine the effect of surface area (the maximum surface area of the wires was $1.6 \times 10^4 \text{ mm}^2$).

After the discharge for the period of desired time, the surface of the iron wires was examined by XPS and compared with the spectra of the surface before the discharge to identify the adsorbed species on the iron surface by the discharge. The species formed in the discharge were identified by emission spectroscopy and mass spectroscopy. A Langmuir probe method was applied to estimate the floating potential of the iron wires during the discharge.

3. RESULTS AND DISCUSSION

3.1. Dependences of Ammonia and Hydrazine Yields on the Discharge and on the Number of Iron Wires

Yields of ammonia and hydrazine were measured to investigate the catalytic effect of iron wires on the synthesis of both compounds. The dependence of the ammonia yield on the discharge time when the number of iron wires placed in the discharge was kept at a constant value is shown in Fig. 1. The ammonia yield increased with increasing discharge time linearly up to 2 h, whether the iron wires were present or absent in the discharge. When the iron wires were placed in the discharge, about twice the amounts of ammonia were obtained than those in the absence of the iron wires. The dependence of the hydrazine yield on the discharge time is shown in Fig. 2. The hydrazine yield increased with increasing discharge

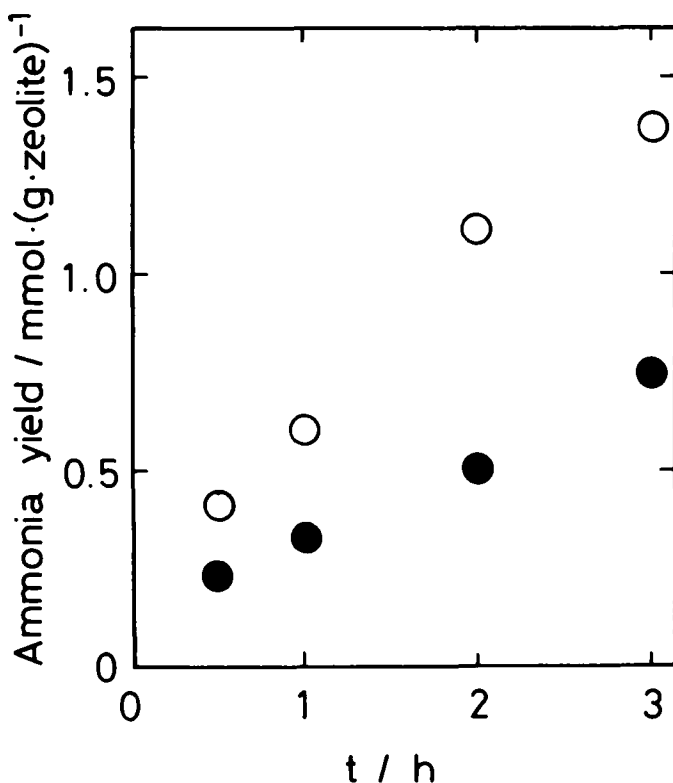


Fig. 1. Dependence of NH_3 yield on the discharge time in the presence (○) or absence (●) of Fe wires in the nitrogen-hydrogen plasma; number of wires, 100 pieces.

time in the presence of iron wires, but the yield did not change in spite of increasing the discharge time when iron wires were not placed in the discharge. When the iron wires were placed in the discharge, the hydrazine yields were two orders of magnitude larger than those obtained in the absence of iron wires in the discharge.

The dependence of the yields of ammonia and hydrazine on the number of iron wires placed in the discharge is shown in Figs. 3 and 4, respectively, to show the effect of surface area of iron wires on the ammonia and hydrazine yields. In both cases, the discharge time was the same, 2 h. The ammonia yield increased with increasing number of iron wires approximately parabolically. Thus the surface of the iron wires contributed to the ammonia formation in the discharge. The hydrazine yield increased with increasing number of iron wires exponentially. The hydrazine yield reached values

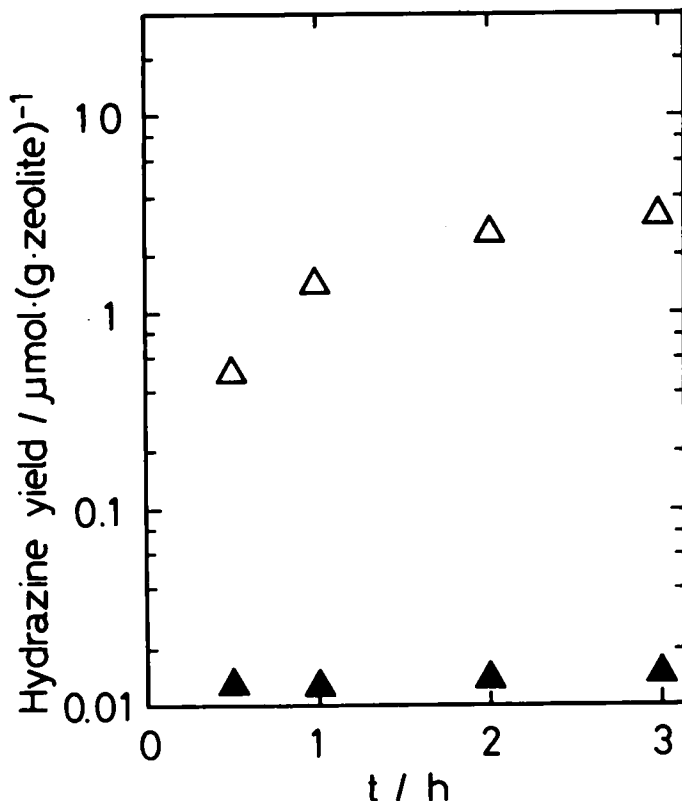


Fig. 2. Dependence of N_2H_4 yield on the discharge time in the presence (Δ) or absence (\blacktriangle) of Fe wires in the nitrogen-hydrogen plasma; number of wires, 100 pieces.

three orders of magnitude larger than those obtained in the absence of iron wires in the discharge. The catalytic effect of iron wires is considerably higher on the hydrazine synthesis than that on ammonia synthesis.

3.2. Temperature Measurement and Characterization of the Iron Surface

The surface area of iron wires placed in the discharge considerably affected the yields of ammonia as well as hydrazine. The iron surface contributed to the formation of ammonia as well as hydrazine in the nitrogen-hydrogen mixture plasma. Therefore, the characterization of the iron surface was carried out by XPS to identify the species on the iron surface. As the surface reaction is controlled by temperature, the surface temperature of the iron wires was estimated using thermocrayon. The iron

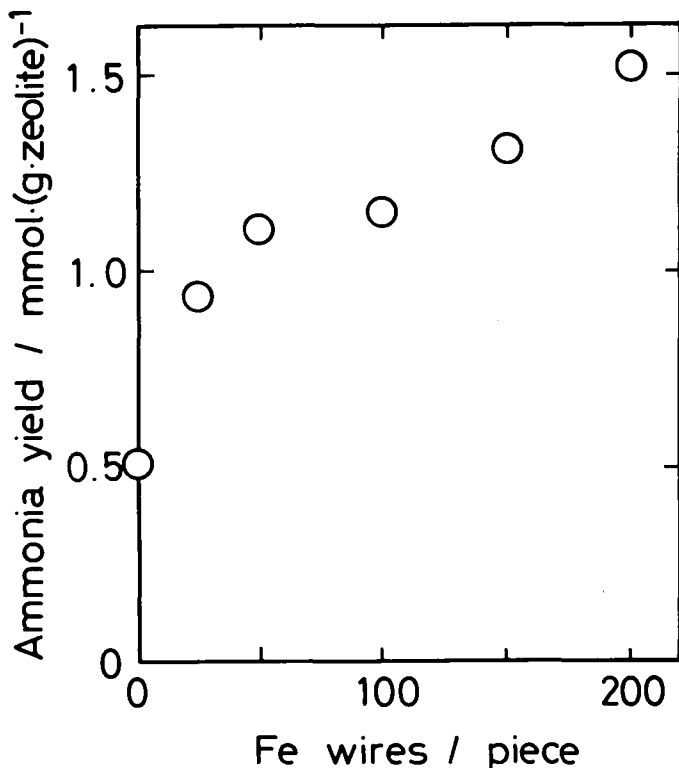


Fig. 3. Dependence of NH_3 yield on the number of Fe wires; discharge time, 2 h.

wires placed in the plasma 150 mm downstream the center of the inductive coil was estimated to be 620 ± 50 K. The surface temperature is approximately the same as that of the catalyst in the Haber-Bosch process.⁽¹⁰⁾

The XPS spectra of $\text{N}1s$ electrons of the iron surface after being placed in the discharges of the nitrogen-hydrogen gas mixture and nitrogen gas are shown in Figs. 5A and 5B, respectively. A strong peak due to adsorbed $\text{NH}_3(\text{a})$ and a shoulder peak due to adsorbed $\text{NH}(\text{a})$ and/or $\text{NH}_2(\text{a})$ were identified on the surface of the iron wires placed in the discharge of the nitrogen-hydrogen gas mixture like on the surfaces of iron single crystal⁽¹¹⁾ and industrial Fe ammonia catalyst which was used in the Haber-Bosch process at 620–670 K (350–400 °C).⁽¹⁰⁾ Since the intensity of the peak due to $\text{NH}_3(\text{a})$ was decreased by Ar^+ ion etching, NH_3 would be weakly adsorbed (perhaps by a physical adsorption). When the iron wires were placed in the discharge of nitrogen, the formation of the Fe–N bond was identified in the XPS spectra as reported previously.⁽⁶⁾

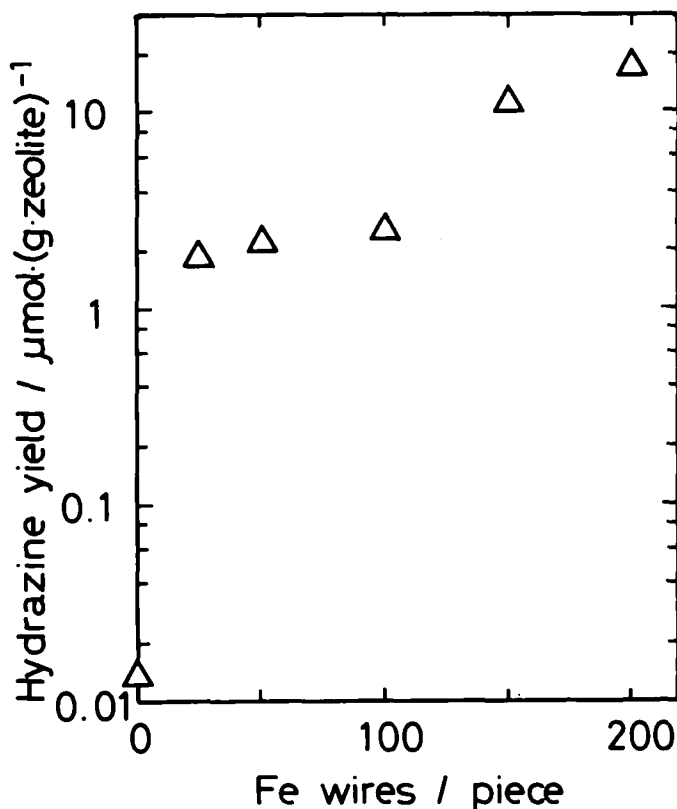


Fig. 4. Dependence of N_2H_4 yield on the number of Fe wires: discharge time, 2 h.

Placing nitrified iron in the hydrogen plasma decreased the intensity of the Fe-N peak, and the N-H peak appeared in the XPS spectra. In this case, NH as well as NH_x^+ ($x = 1-4$) ions were identified in the hydrogen plasma by emission spectroscopy and mass spectroscopy.⁽⁷⁾ This suggests that interaction between chemically bound nitrogen on the iron surface and hydrogen atom in the plasma takes place. The adsorption of NH_x ($x = 0-3$) on the iron surface followed by desorption of ammonia to form iron nitride during the ion nitriding of iron has been proposed as a reaction scheme based on mass spectrometric diagnostics.⁽¹²⁾

3.3. Dependence of Ammonia and Hydrazine Yields on Catalyst Temperature

The contribution of iron surface to the catalytic effect of iron is due to the surface coverage of ammonia. As the coverage depends on the surface

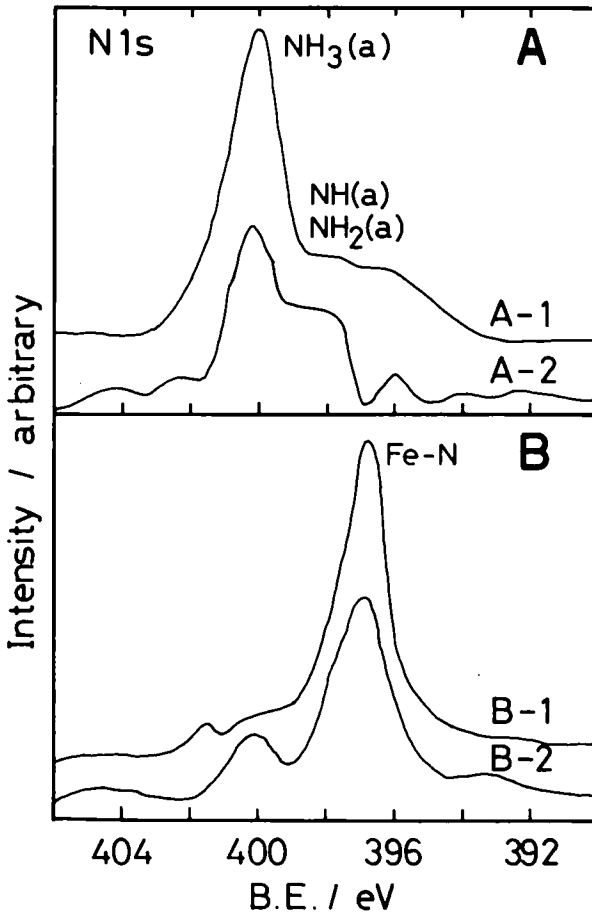


Fig. 5. XPS spectra due to N1s electrons of Fe catalyst placed in the nitrogen-hydrogen plasma (A) and the nitrogen plasma (B): discharge time, 2 h in A-1 and B-1; Ar⁺ ion etching time, 5 min in A-2; exposure time in hydrogen plasma, 15 min in B-2.

temperature, the ammonia and hydrazine yields were measured with changing temperature of iron wires in the discharge using external heating. The dependence of ammonia and hydrazine yields on temperature is shown in Fig. 6. The ammonia yield was maximum around 700 K, then decreased with increasing temperature. The hydrazine yield decreased monotonously with increasing temperature.

Yields of ammonia as well as hydrazine depended on the temperature of iron wires placed in the discharge as expected. Therefore, the XPS spectra of N1s electrons of the iron surface after it was placed in the discharge at

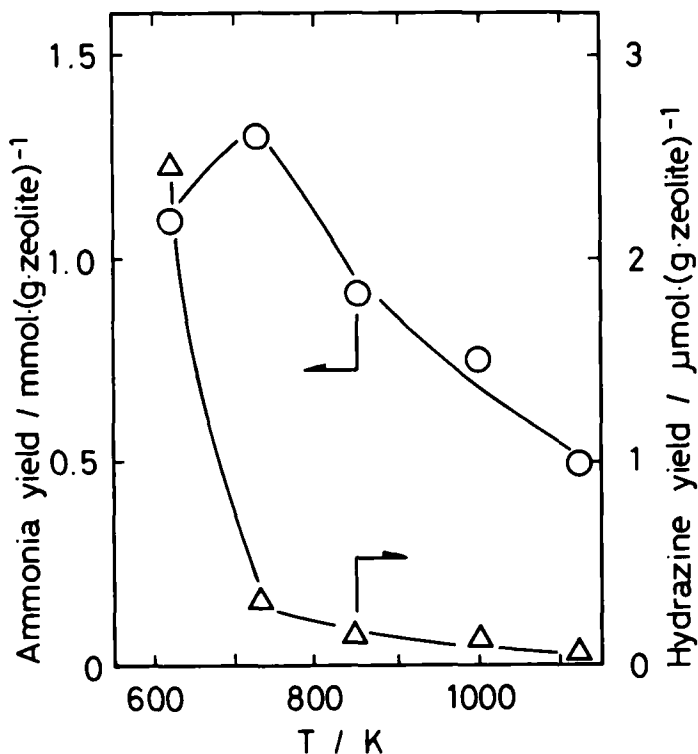


Fig. 6. Effect of Fe catalyst temperature on NH_3 (○) and N_2H_4 (△) yields; discharge time, 2 h; number of wires, 100 pieces.

desired temperatures were measured. These spectra are shown in Fig. 7. Both the peaks due to adsorbed ammonia and the Fe-N bond were identified at temperatures between 620 and 730 K. When the temperature was higher than 850 K, only the Fe-N bond was identified in the spectra. The adsorption of ammonia on the iron surface would accelerate the formation of ammonia as well as hydrazine, as the correlation between the yields of both compounds and the adsorption of ammonia on the iron surface indicated.

3.4. Emission Spectroscopy and Mass Spectroscopy of the Nitrogen-Hydrogen Plasma

To clarify which kinds of species in the plasma contribute to the ammonia and hydrazine formation, the emission spectra and mass spectra were obtained. The electronic transitions identified in the nitrogen-hydrogen

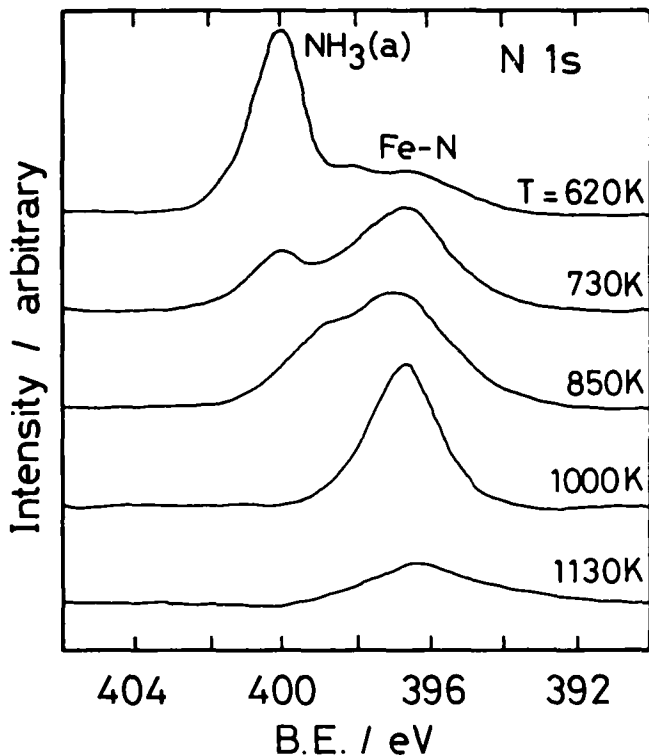


Fig. 7. XPS spectra due to N1s electrons of Fe catalyst after using at various catalyst temperatures; discharge time, 2 h.

plasma are given in Table I. The $A-X$ electronic transition of NH and Balmer lines due to the hydrogen atom were identified in the plasma together with the first and the second positive systems of N_2 and the (0-0) sequence

Table I. Electronic Transitions Observed in Emission Spectra from Nitrogen-Hydrogen Plasma

Species	Transitions observed at 700-200 nm	
N_2	$B^3\Pi_g - A^3\Sigma_u^+$	$\Delta v = 3 \quad (v' \leq 3)$
	$C^3\Pi_g - B^3\Pi_g$	$\Delta v = -4-3 \quad (v' \leq 4)$
N_2^+	$B^2\Sigma_u^+ - X^2\Sigma_g^+$	$\Delta v = 0 \quad (0-0)$
NH	$A^3\Pi - X^3\Sigma^-$	$\Delta v = 0 \quad (0-0)$
H	Balmer series	$H\alpha, H\beta$

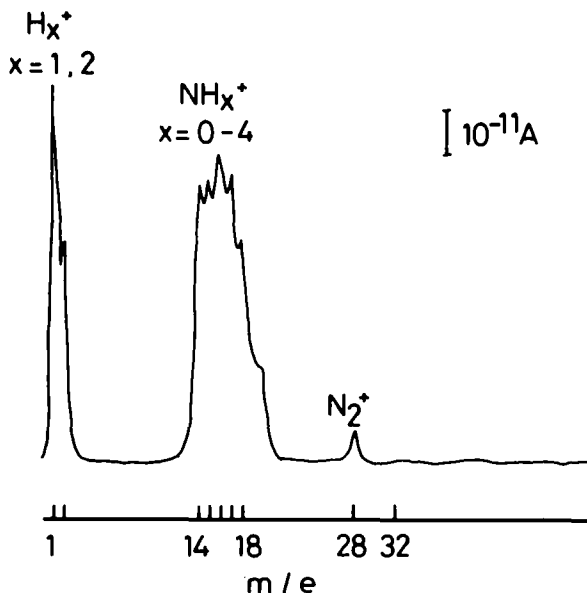


Fig. 8. Mass spectrum of nitrogen-hydrogen plasma.

of the first negative system of N_2^+ . NH_2 , which was considered as an ammonia precursor along with NH ,⁽⁴⁾ could not be identified by emission spectroscopy.

The mass spectra of the nitrogen-hydrogen plasma sampled from downstream of the gas flow by the same way as reported elsewhere⁽¹³⁾ are shown in Fig. 8. N^+ , NH^+ , NH_2^+ , NH_3^+ , as well as NH_4^+ were identified with N_2^+ , H^+ , and H_2^+ . In this case, only ions which were extracted by applying negative potential against the plasma were detected directly without ionization in the mass analyzer, so the resolution was not so high.⁽¹⁴⁾ These NH_x^+ ions are considered as ammonia precursors in addition to N_2^+ ion. These species adsorb on the iron surface.

3.5. Application of Langmuir Probe Techniques to the Nitrogen-Hydrogen Plasma

A Langmuir probe was set in the discharge of the nitrogen-hydrogen gas mixture to estimate the floating potential on the iron surface and the plasma potential.^(15,16) In this case, iron wires were used as a reference electrode. The $I-V$ characteristic curve obtained is shown in Fig. 9. The floating potential as well as the plasma potential were estimated to be -43

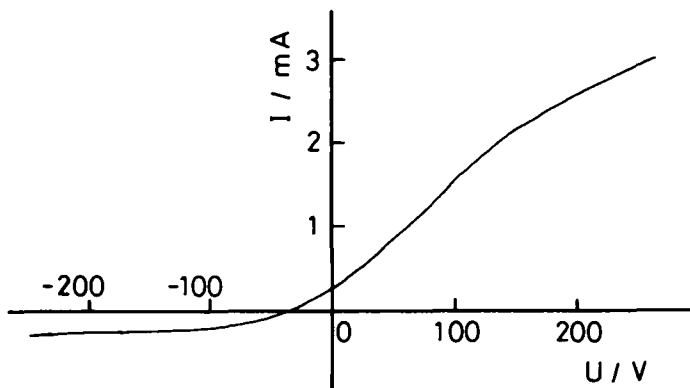


Fig. 9. Langmuir probe characteristics of nitrogen-hydrogen plasma.

and 145 V, respectively. Thus the iron wires were negatively biased against the plasma.

3.6. Catalytic Effects of Iron Wires on the Syntheses of Ammonia and Hydrazine in the Nitrogen-Hydrogen Plasma

From the results obtained in the previous sections, the catalytic effect of iron wires on the syntheses of ammonia and hydrazine in the nitrogen-hydrogen plasma was found. In the formation process of ammonia from nitrogen-hydrogen plasma using iron as the catalyst, nitrogen atoms adsorbed on the iron surface by the dissociative adsorption of excited nitrogen molecules⁽⁴⁾ or nitrogen molecular ions⁽⁵⁾ reacted with hydrogen atoms or molecules formed in the plasma. In the present work, both reaction schemes were supported.

The electron density in a similar plasma was estimated to be 10^{10} cm^{-3} by a double-probe technique.⁽¹³⁾ Thus, the degree of ionization was an order of magnitude of 10^{-7} . The dissociative adsorption of neutral species, N_2 as well as NH_x , is considered as the primary reaction process. As the iron wires were negatively biased against the plasma, the bombardment of iron wires by positive N_2^+ ions as well as NH_x^+ ions which were prepared in the discharge, and the neutralization of ions and dissociative adsorption were also supposed. However, the degree of ionization was considerably too low to allow the reaction to proceed under this scheme.

In addition to the two proposed reaction schemes, the formation of ammonia by the reaction between iron nitride (Fe_3N) identified on the iron surface and hydrogen atoms in the discharge was considered as the other

ammonia formation process, though the ammonia yield through this process may not be so high.

In the present work, the product yield of hydrazine increased two or three orders of magnitude by the placement of iron wires in the discharge than that obtained in the absence of iron wires, though the yield of ammonia increased only two or three times. The results obtained by spectroscopic investigations suggested that hydrazine was formed from adsorbed ammonia on the iron wires by the reaction with NH radicals formed in the nitrogen-hydrogen discharge as suggested in the literatures.^(17,18) On the other hand, hydrazine would also be formed by the reaction between adsorbed NH₂ (a) and NH₂ radicals in the discharge, because the adsorption of NH₂ on the iron surface was identified in the XPS of N1s electrons (Fig. 5A). Moreover, the surface of iron wires was covered with iron oxide (Fe₂O₃) which is a basic oxide like NaOH and MgO. As the introduction of NaOH or MgO into the discharge increased the hydrazine yield,^(19,20) the catalytic effect of iron on hydrazine synthesis was similar to that in NaOH as well as MgO.

3.7. Catalytic Effect of the Plasmas on the Synthesis of Ammonia and Hydrazine

The catalytic effects of iron wires discussed in the previous sections are mainly based on the surface reactions on iron wires under the plasma conditions. On the other hand, the energy for reactions, as well as an activation energy up to 400 kJ mol⁻¹ (≈ 4 eV), can be supplied by the plasma. The strongly endothermic reactions can take place at low temperature (N₂ → 2N, for example). This is known as a plasma catalytic effect.^(1,21) In the discussion of the catalytic effects of iron wires, it is necessary to discuss the effects of surface reaction separately from plasma conditions, namely the reaction has to be carried out without discharge, on the reactions of ammonia as well as hydrazine syntheses. The catalytic effects of industrial Fe ammonia catalysts were investigated by means of XPS in nitrogen-hydrogen gas mixture (1 atm) at 620–670 K (350–400 °C).⁽⁹⁾ The conclusion that dissociative chemisorption of nitrogen on the catalyst surface is the rate-determining step is supported by the identification of adsorbed atomic nitrogen on the surface.

To investigate the additional effects of plasma conditions on ammonia as well as hydrazine syntheses using iron wires as the catalyst indirectly, the ammonia and hydrazine yields were measured in the nitrogen-hydrogen gas mixture without discharge and compared with the results obtained with discharge. When the discharge was not applied, the temperature of iron wires was kept at 620 K by external heating. Yields of ammonia and

Table II. Ammonia and Hydrazine Yields Obtained with or without Discharge when the Iron Wires Were Placed in the Nitrogen-Hydrogen Gas Mixture^a

	NH ₃ (mmol g ⁻¹)	N ₂ H ₄ (μmol g ⁻¹)
With discharge	1.1	2.5
Without discharge	0.05	<0.01

^aNumber of Fe wires, 100 pieces; catalyst temperature, 620 K; exposure time, 2 h.

hydrazine in both cases are given in Table II. By the application of discharge, the yields were two orders of magnitude for ammonia and four orders of magnitude for hydrazine higher than those obtained when the discharge was not applied. The adsorption of considerably large amounts of NH₃ was identified on the iron surface with discharge as shown in Fig. 5A. When the discharge was not applied, only the weak adsorption of N₂ was identified, like that observed on the starting materials before using them as the catalyst. In this case, XPS peaks of N1s electrons due to adsorbed NH_x (x = 1-3) and Fe-N bond (or chemisorbed N atom) could not be found.⁽¹¹⁾

The difference in product yields with and without discharge is determined and it is due to the excitation, dissociation, and/or ionization of nitrogen and hydrogen molecules in the discharge. The excitation, dissociation, and/or ionization of molecules in the discharge affect the dissociative adsorption of nitrogen on the iron surface and the formation of N-H bond on the iron surface. Both plasma catalysis and surface catalysis go hand in hand in promoting the synthesis of ammonia as well as hydrazine.

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