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HYDRAZINE SYNTHESIS BY N_2-HYDROGENATION ON SOLID SURFACES WITH GLOW DISCHARGE*)

By

Koshiro MIYAHARA**)

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Abstract

Hydrazine synthesis by N_2-hydrogenation on solid surface was examined with various solid materials. Nitrogen molecule excited by glow discharge and its interaction with hydrogen source material held on solid surface were concluded to be vital for the steadily synthesis at room temperature.

Ammonia with a little amount of hydrazine was formed on solid surface from discharging H_2/N_2 mixture with rate of 0th order dependence on the total pressure. The rate increased and the fraction of hydrazine in product decreased, with rise of the mixing ratio of H_2 to N_2 from zero to *ca.* 3. Such a course of the reaction of H_2/N_2 mixture was nearly independent of the sort of solid material.

With N_2 gas alone, OH groups chemisorbed on the solid surface was selectively used for the formation of hydrazine, however, the reaction was limitted in the early stage of the discharge. The steady formation of hydrazine from N_2 was performed by the interaction of plasma of CH_4/N_2 mixture with solid surface or that of N_2 plasma with solid surface covered with higher hydrocarbons. A little amount of CN compounds but not ammonia was formed in this case and the product should be trapped off immediately after the interaction to suppress the formation of ammonia and CN compounds and to obtain hydrazine with high selectivity. Ammonia was useless for hydrazine synthesis with glow discharge, as it was simply decomposed and preferentially forms CN compounds under glow discharge in the presence of hydrocarbon. Monosilane was also useless as a hydrogen source for hydrazine synthesis from N_2, because of its high facility of decomposition in plasma to give hydrogen gas.

In conclusion, the effect of glow discharge for hydrazine formation is based on the formation of excited N_2 molecule (presumably $A^3\Sigma u^+$), which collides with OH groups or hydrocarbon held on the solid surface and drives out excited H atoms, presumably proton and/or radical, and are quenched as hydrazine molecule by the wall effect of the solid. The steady formation of ammonia from plasma of H_2/N_2 mixture may be caused by the simple wall effect of solid surface.

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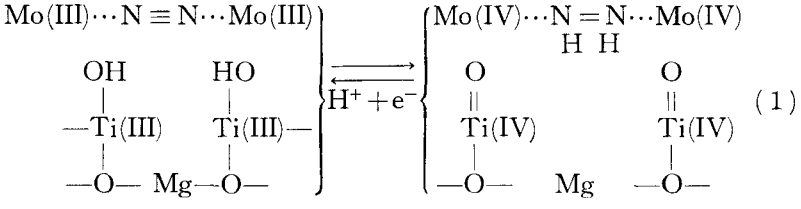
**) Research Institute for Catalysis, Hokkaido University, Sapporo, 060 Japan.

Introduction

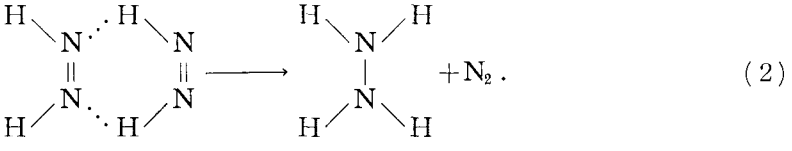
The direct synthesis of hydrazine by heterogeneous catalysis in gas phase has been an outstanding problem of N_2 hydrogenation since the development of ammonia synthesis over iron catalyst. With respect to this problem, hydrogenation of molecular nitrogen to hydrazine has been investigated by means of the decomposition of metal complexes of molecular nitrogen,[1] the photocatalysis with wet titania in nitrogen atmosphere[2] and catalysis by metal hydroxide in liquid phase[3,4] *etc.* Summerizing the results of these experiments, we see that (1) the activation of molecular nitrogen by its coordination to appropriate metal ions and (2) the protonation of this excited nitrogen molecule, are indespensable for the direct synthesis of hydrazine. Furthermore, (3) the redox cycle of metal ions should be taking place to realize the process as catalysis.

This conclusion is illustrated by the mechanism proposed by Shilov *et al.*[4] for the system of mixed hydroxides of molybdenum, titanium and magnesium in a liquid phase as



(1)

Shilov *et al.*[4] have succeeded to realize the second and third conditions mentioned above by means of dissolution of Na-amalgam in alkaline medium. Schrauzer[5] has additionally proposed that the N_2-hydrogenation by Scheme (1) is two electrons-process to give N_2H_2 and hydrazine might be formed by the disproportionation of N_2H_2 as



(2)

The scheme (1) suggests for the present a possibility of hydrazine synthesis on solid surfaces as follows. It is much suggestive for the molecular activation of nitrogen on solid surface, that the catalytic activity for N_2-hydrogenation in the studies mentioned above[2~5] has been referred to that for

hydrogenation of acetylene, an electronic isostar of N_2 molecule, and other unsaturated hydrocarbons. The present author has long investigated the heterogeneous catalysis of olefines over various solid surfaces. Transition metals have high catalytic activity for olefine hydrogenation and isomerization *etc.*, however, their fresh surfaces are highly active, too, for dissociative adsorption and, accordingly, polimerization of olefine. On the other hand, some metal oxides and sulfides, *e.g.* MoO_3 supported on TiO_2, MgO and MoS_2 *etc.*, have been found to catalyze the same reactions of olefine, activating olefine in its molecular state[6~7] to cause the associative mechanism.[7~9] Additionally, the fact that the surfaces of metal oxides or sulfides evacuated at *ca.* 500°C are abundant in chemisorbed OH or SH groups, seems to be favorable to realize the scheme (1) on solid surface.

The present experiment was, thus, started with metal oxides as catalysts, and glow discharge was applied to reactant gas for the convenience to supply proton and electron onto the surface of solid insulator.[10]

Experimental

The reaction appartus[10] was a usual circulation system of *ca.* 220 cm^3 volume as shown in Fig. 1, and the rate of circulation was more than 1×10^3 cm^3/min. All stop valves in the system were of greeseless, otherwise the apparatus could not be evacuated due to hydrazine dissolved into greese. The reaction vessel was a quartz U-tube of 6 mm inner diameter, in which

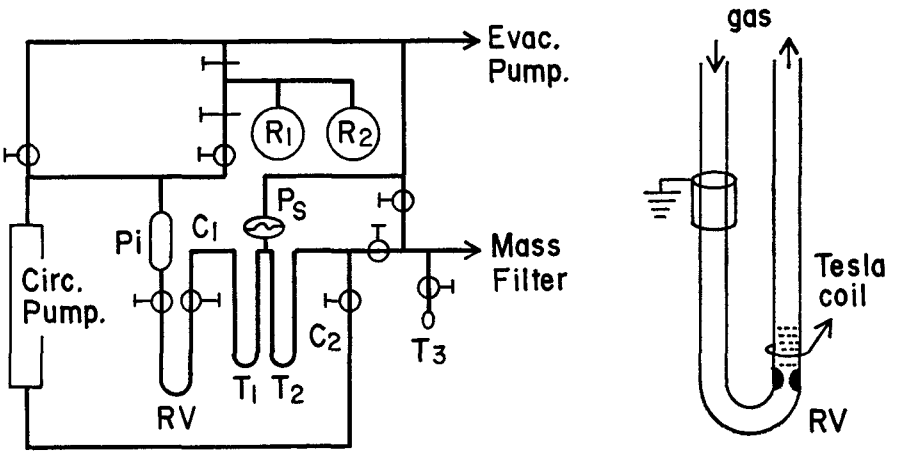


Fig. 1. Diagram of reaction system.
RV: quartz U tube reaction vessel, R: gas reservoir, C: stop valve, T: cold tap, P_S: strain gauge, P_i: Pilanyi gauge.

the catalyst bed was set with its length less than *ca.* 1 cm, as shown by RV in Fig. 1.

The silent discharge from a Tesla coil of *ca.* 16 WH was applied to the reactant gas of less than *ca.* 1×10^3 Pa by setting the poles of discharge so as to limit the glow of discharge to the gas inlet side of the catalyst bed. The intensity of the glow discharge was changeable by sliding the poles of Tesla coil and earth. The total pressure of gas was followed by strain gauge, P_s, TOYODA DD-102A, while Pilanyi gauge, Pi, was used for the flash desorption (FD) experiment.

A mass filter, NAG-515 of NEVA, was used for the gas analysis at $2.5\sim4.0\times10^{-5}$ Pa. The reaction product trapped at $-195°C$ contained water, carbon monoxide, dioxide and hydrocarbon *etc.*, and, hence, $^{15}N_2$ was used for the reaction to make easy the gas analysis. In this mass filter with an ionization chamber causing abundant ion-molecule reactions, majority of hydrazine was decomposed to give N_2 and ammonia and N_2 was also formed from ammonia alone. And, hence, we can analyse water, ammonia and hydrazine in the trapped product of the $^{15}N_2$ reaction, on the basis of peak heights at m/e=17,18 and 30 excluding the effect of carbon monoxide, dioxide and hydrocarbon *etc.* to the mass spectra. The contribution of nitrogen compounds to the mass spectra can be detected by the shifts of their peaks by $\Delta(m/e)=-1$ or -2, caused by the change of reactant nitrogen from $^{15}N_2$ to $^{14}N_2$. The utility of the mass filter for the analysis of hydrazine and ammonia was further ascertained by the uses of their mixtures and the trap T_3, shown in Fig. 1, charged with $KMnO_4$ crystallites, with which only hydrazine of the reaction product was completely changed to N_2 at room temperature.

The catalyst was usually pretreated by flash desorption with rise of temperature from room one to 600°C during 10 min. and cooled to room temperature under evacuation. After the introduction of a known amount of reactant to the reaction system, the reaction was started by applying glow discharge, without which any reaction was absent. After the reaction of *ca.* 10 min with cold trap T_1, the valves C_1 and C_2 in Fig. 1 were closed for the complete evacuation of the trap. The product condensed in the trap T_1 was then outgassed by transferring it into trap T_2. The completion of this evacuation or outgassing was ascertained by the disappearance of the peak at m/e=30 in the mass spectrum observed with fully opened leak valve of the mass filter. The content of trap T_2 was finally vaporized in traps, T_1 and T_2, of 22 cm^3 volume to measure its amount by P_s and then flowed into the mass filter. The use of $^{15}N_2$ gas and such a careful out-

gassing of the condensed product enabled us to perform the accurate gas analysis of the trapped product.[10]

Results and Discussions

(*A*) *Variation of solid materials.*

i) Metal oxides

The results of the experiment with powdered metal oxides and a gas mixture of $H_2/^{15}N_2 \simeq 2$ are given in Table 1.[10] The mixed solids were made by impregnation of main oxide with aqueous solution of appropriate metal salts, except their halogenides. The mole ratios of metal ions in mixed oxides are given in Table 1 with parenthesis. The dried solid sample was calcined in air at 600°C and *ca.* 0.1 g was charged in the reaction vessel with a little amount of quartz wool and evacuated up to 600°C for 10 min to get the flash desorption spectrum. Under the glow discharge, the reaction of $H_2/^{15}N_2$ mixture was steady and 0th order with respect to the total pressure, while only a slight decrease of the pressure was observed in the early stage of the reaction with $^{15}N_2$ alone. Table 1 shows the real possibility of the hydrazine synthesis over solid surfaces, in spite of its poor

TABLE 1. N_2-hydrogenation on powdered metal oxide catalysts with $H_2/^{15}N_2 \simeq 2$ mixture.

Metal oxide	Activity $-\Delta P/\Delta t$ (Pa/s)	Selectivity ($^{15}NH_3 : {}^{15}N_2H_4 : CH_4{}^{15}N_2$ mol%)					
		with $H_2/^{15}N_2$ mixture			with $^{15}N_2$ alone		
None	0.18	100	0	2	—	—	—
SiO_2 gel	0.20	87	11	2	0	20	80
$MoO_3/TiO_2/Mg(OH)_2$ (0.04/1/20)	0.21	96	4	0	0	9	91
am $TiO_2/Mg(OH)_2$ (1/20)	0.28	91	9	0	0	42	58
MoO_3/Mg oxalate (1/20)	0.28	86	0	14	0	0	100
am TiO_2	0.25	80	11	9	0	0	100
$Mg(OH)_2$	0.32	92	8	0	0	80	20
Al_2O_3	0.20	72	28	0	0	46	54
SiO_2/Al_2O_3 (commercial)	0.18	88	12	0	0	12	88
SiO_2/MgO (1/1)	0.23	23	17	60	8	24	68

selectivity in the steady reaction. The products under the discharge of $^{15}N_2$ alone are different from each other depending on the sort of solid, especially with respect to the formation of diaziridine, $CH_2{}^{15}N_2H_2$,[5] instead of hydrazine. The oxides of Mo and Ti have been reported[8] as active catalysts for olefine metathesis reactions, indicating that metal carbenes are formed and stabilized on their surfaces. In fact, hydrocarbon up to C_6 was formed in the present experiment under the glow discharge of H_2 alone, irrespective of the sort of metal oxide. This fact indicates the incorporation of carbonaceous impurity of the metal oxides. The hydrogen source for the hydrogenation of N_2 alone might be OH groups chemisorbed on the metal oxide surface, which is called as surface-OH in what follows. The preferential formation of diaziridine under the discharge of N_2 alone indicates that molecular nitrogen excited by glow discharge is scavenged by carbene easier than its hydrogenation with surface-OH into hydrazine. The high selectivity of diaziridine formation from H_2/N_2 mixture on SiO_2/MgO shown in Table 1 may be due to SiO_2 being derived from alcoholate. Anyway, the formation of N_2 compounds in these cases might be surface reaction.

Hydrogen cyanide and/or amino acids, reported[11] as to be formed remarkably from the gas mixture of ammonia and hydrocarbon under the discharge or over heated silica gel were practically absent in the present experiment with liquid nitrogen trap T_1. This was concluded on the basis of mass spectra, which showed none of visible change, except the peaks of NH_3, N_2 and CH_4N_2, by the change of reactant nitrogen from $^{15}N_2$ to $^{14}N_2$.

The activity in the reaction of H_2/N_2 mixture was mainly affected by the intensity of the glow discharge as well as the rate of gas circulation, but not by the surface area or the sort of solid. Furthermore, it was noted by the flash desorption after the reaction that a large amount of product was held on the powdered solid surface during the reaction. The solid samples were, hence, changed to quartz pieces and MgO (100) single crystallites (from Tateho Chem. Co. Ltd.), both of 10~16 mesh. They were calcined in air at 1200°C for an hour or more and, furthermore, modified by various metal oxides by wetting their 0.6 g with an aqueous solution of metal salts (5 mg/cm^3) and then calcined at 600°C. With these solid samples, the effects of adsorption and incorporation of carbonaceous impurity were expected to be suppressed. The results are given in Table 2 and Fig. 2,[10] where quartz, MgO and those modified by various metal oxides behaved quite similarly to each other. We see in Table 2 that the hydrazine formation under discharge of $^{15}N_2$ alone became much selective by suppresing the formation of diaziridine. Figures 2 shows, furthermore, that the activity

TABLE 2. $^{15}N_2$-hydrogenation on quartz pieces and MgO(100) single crystallites.

Catalyst	modified with	$H_2/^{15}N_2$ mol ratio	Activity $-\Delta P/\Delta t$ (Pa/s)	Selectivity ($^{15}NH_3 : {}^{15}N_2H_4 : CH_4$ $^{15}N_2$ mol%)					
				with $H_2/^{15}N_2$ mixture			with $^{15}N_2$ alone		
Quartz	None	1.48	0.22	79	21	0	8	86	6
	V	1.68	0.21	74	26	0	10	85	5
	Cr	1.37	0.19	85	15	0	0	99	1
	Co	1.25	0.20	73	27	0	14	84	2
	Ti	1.32	0.15	58	42	0	0	96	4
	K	1.19	0.14	64	36	0	0	98	2
MgO	None	1.39	0.15	74	26	0	16	84	0
	Mo	1.61	0.13	83	17	0	0	68	2
	V	1.09	0.15	76	24	0	0	98	2
	Cr	1.35	0.17	77	23	0	7	89	4
	Co	1.61	5.13	66	34	0	0	96	4
	Ti	1.92	0.15	77	23	0	4	92	4
	K	1.45	0.22	75	25	0	12	86	2

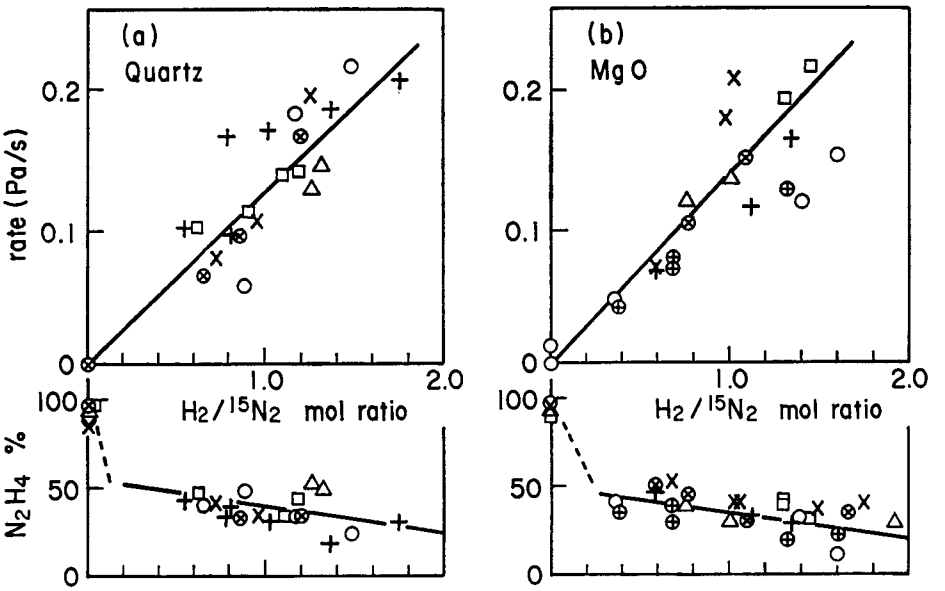


Fig. 2. The dependence of the activity and selectivity for hydrazine synthesis over a) quartz pieces and b) MgO (100) single crystallites.
○ : unmodified, ⊕ : Mo, ⊗ : V, + : Cr, × : Co, △ : Ti and □ : K.

and hydrazine selectivity in the case of $H_2/^{15}N_2$ mixture depend uniquely on the mixing ratio of H_2 to $^{15}N_2$, irrespective of the sort of solid surface, indicating that $^{15}N_2$-hydrogenation under discharge of $H_2/^{15}N_2$ mixture is affected overwhelmingly by the simple wall effect of the solid surface on the plasma of $H_2/^{15}N_2$ mixture.

The assumed high selectivity of surface-OH on metal oxide for hydrazine formation from N_2, was further ascertained by the experiment with MgO (100) single crystallites as follows.[12] The glow discharge of $^{15}N_2$ alone or its mixture with H_2 and successive flash desorption were repeated on the same MgO sample. The results are given in Table 3,[12] where the parenthesized figures give the total amount (10^2 Pa•cm^3) of trapped product obtained by *ca*, 10 min reaction or by flash desorption up to 600°C. We see that the amount of trapped product from $^{15}N_2$ alone, the most of which was hydrazine, decreased and the selectivity of hydrazine formation from $H_2/^{15}N_2$ mixture decreased, too, by repetition of the reaction and flash desorption. This result may be caused by the reduction of surface-OH. The amount of

TABLE 3. Reproducibility of $^{15}N_2$-hydrogenation on MgO crystallites.

Solid	Gas		Trapped product			
	$H_2/^{15}N_2$ ratio	$-\Delta P/\Delta t$ (Pa/s)	$\Delta n/\Delta t$ $\left(10^2 \frac{Pa \cdot cm^3}{min}\right)$	$^{15}NH_3$: $^{15}N_2H_4$: CH_4 (Mol %)	$^{15}N_2$	
MgO	$^{15}N_2$ alone	None	(0.68)	6	89	5
	0.69	0.11	5.87	80	18	2
	1.00	0.13	8.74	90	9	1
	600°C FD		(0.88)	38	62	0
	$^{15}N_2$ alone	None	(0.35)	13	81	4
	0.60	0.11	6.57	92	3	5
	600°C FD		(0.61)	40	60	0
	$^{15}N_2$ alone	None	(0.29)	7	88	5
	0.92	0.12	7.57	97	2	1
	600°C FD		(0.44)	50	50	0
K/MgO	$^{15}N_2$ alone	None	0.03	0	75	25
	1.63	0.35	—	100	0	0
K/MgO (H_2O, 500°C)	$^{15}N_2$ alone	None	0.03	22	79	0
	0.72	0.19	—	100	0	0

surface-OH on MgO crystallites was, thus, intentionally reduced by the treatment with KOH aqueous solution and calcination at 600°C, with which it was expected that the surface-OH is ion-exchanged to form surface-OK.[13] The hydrazine selectivity on the KOH-treated MgO, K/MgO, was hardly recovered by heating it in water vapor at 500°C. The absence of hydrazine in the case of $H_2/^{15}N_2$ mixture on K/MgO is probably ensured by the promotion effect of surface potassium for the dissociative adsorption of $^{15}N_2$, as well known in the ammonia synthesis over iron catalysts.[14]

ii) Metals and metal sulfides — proof of the simple wall effect of solid surfaces on the plasma of H_2/N_2 mixture.[12]

If the N_2-hydrogenation with discharging H_2/N_2 mixture on solid were caused by a simple wall effect of solid surface, the results of metal oxides mentioned above should be reproduced with solid samples other than metal oxide. Metal tips of Pt, Ni. Fe, Ru, Si Zr, and alloys, am-$Ti_{30}Ni_{66}$, am-$Pd_{0.35}Zr_{0.05}H_{1.0}$, $LaNi_5$ and stainless steel (SUS 304), MoS_2 single crystallites and CoS powder were examined. The results with the reaction of $H_2/^{15}N_2$ mixture were similar to those with metal oxides given in Table 2. In the case of CoS powder, sulfur oxides and/or carbon oxides, but none of nitrogen compounds and hydrocarbon were found in the condensed product of the flash desorption carried out after the reaction. This result indicates the inactivity of CoS surface for adsorption of nitrogen compounds and/or their precauser, makeing sure the simple wall effect of CoS surface for the N_2-hydrogenation into ammonia under discharge of H_2/N_2 mixture, in conformity with its complete inactivity as a olefine hydrogenation catalyst[15] and the present expectation for the simple wall effect on the ammonia formation from H_2/N_2 mixture.

(*B*) *Variation of hydrogen sources*

Summerizing the results of foregoing experiments, we see that excited N_2 molecule is hydrogenated selectively into hydrazine by surface-OH and/or -SH, but mainly into ammonia by H_2 gas. The variation of hydrogen sources was investigated with respect to hydrazine formation from N_2 gas. Table 4[12] gives the result obtained with pieces of $LaNi_5$ alloy, which is known as a good hydrogen reservoir easily liberating hydrogen at room temperature. The first and the third series of reaction in Table 4 were carried out after the flash desorption of the alloy up to 600°C and gave results quite similar to those mentioned in the foregoing section (A). Curves in Fig. 3 are the flash desorption spectra obtained by FD experiments a) *etc.* given in Table 4. The gas evolved at temperatures below 350°C was

nitrogen and its compound, while above 350°C solely hydrogen was evolved. We see by curves b) and d) that the alloy absorbed hydrogen during the glow discharge of $H_2/^{15}N_2$ mixture even at room temperature and at low partial pressure of hydrogen. Hydrogen was, thus, charged into the alloy by applying glow discharge of H_2 alone circulating at *ca.* 7×10^3 Pa and at room temperature until an equilibrium hydrogen pressure of *ca.* 10 Pa was attained. The $^{15}N_2$-hydrogenation was carried out after evacuation at room temperature. We see in Table 4 that considerable amount of ammonia was formed with $^{15}N_2$ alone at room temperature as compared with the same reaction over the alloy without dissoloved hydrogen. At 100°C, hydrogen was liberated notably into gas phase and we had high selectivity for ammonia formation as much as the reaction with $H_2/^{15}N_2$ mixture on the alloy without dissoloved hydrogen. This result indicates that the hydrogen diffused onto the surface of the alloy was preferentially used for ammonia formation.

Relating to the fact that diaziridine was formed with glow discharge of

TABLE 4. $^{15}N_2$-hydrogenation on $LaNi_5$ (0.9 g) at room temperature.

Pretreatment	Gas		Trapped product			
	$H_2/^{15}N_2$	$-\frac{\Delta p}{\Delta t}\left(\frac{Pa}{s}\right)$	$\frac{\Delta n}{\Delta t}\left(10^2\frac{Pa\cdot cm^3}{min}\right)$	$^{15}NH_3$	$^{15}N_2H_4$	CH_4 $^{15}N_2$
H_2 flashed	600°C FD	a)	(0.18)	0	99	1
	0.45	0.04	4.11	80	17	3
	1.78	0.17	13	91	9	0
	3.32	0.16	11.3	92	7	1
	600°C FD	b)	(0.35)	52	48	0
H_2 charged	$^{15}N_2$ alone	(r. t.)	(0.35)	36	61	3
		(100°C)	3.89	78	19	3
	0.11	0.02	1.47	63	35	2
	4.17	0.15→2.10	11.38	94	6	0
	600°C FD	c)	(0.29)	50	50	0
H_2 flashed	$^{15}N_2$ alone		(0.09)	16	81	3
	0.15	0.01	1.36	70	28	2
	3.12	0.15	11.3	93	7	0
	600°C FD	d)	(0.35)	78	22	0

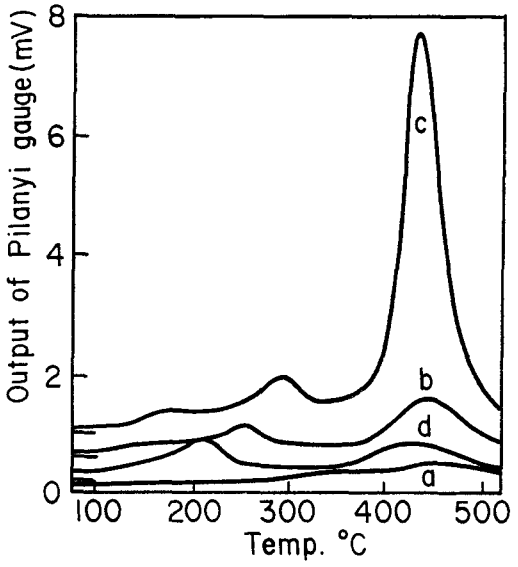


Fig. 3. Flash desorption spectra obtained by FD-experiments with $LaNi_5$ alloy given in Table 4. a): Fresh alloy, b): alloy treated with descharging $H_2/^{15}N_2$ mixture, c): alloy treated with discharging H_2 and d): alloy evacuated at 600°C and used with discharging $^{15}N_2$.

N_2 alone over powdered metal oxides, the reaction of $^{15}N_2$ with CH_4 was examined.[12] The time course of the reaction of discharging $CH_4/^{15}N_2$ mixture at 6.7×10^2 Pa total pressure was given in Fig. 4 as well as Table 5, where the results of reactions with various gas mixtures on the same solid were summerized. Methane was dissociated by the discharge to give hydrogen gas, as seen in Fig. 4, while the trapped product mainly consisted of C_2- and/or higher hydrocarbons and hydrazine, but not ammonia, as seen in the 2nd run of reaction in Table 5. A little amount of carbon dioxide and $R\cdot C^{15}N$ ($R=H$, C_1 and C_2) was formed simultaneously, as given in the parenthesis. We see, furthermore, in the successive run of reaction with $H_2/^{15}N_2$ mixture that the selectivity for hydrazine for-

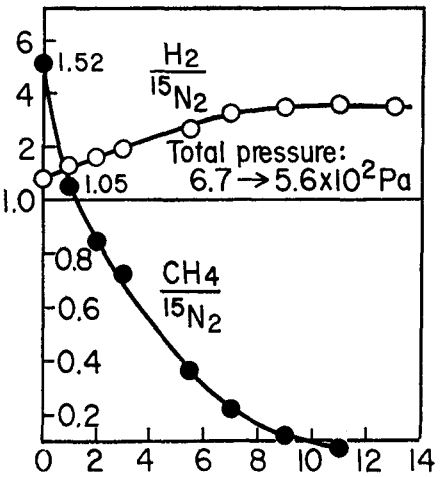


Fig. 4. Time courses of reaction of $CH_4/^{15}N_2$ mixture on $LaNi_5$ alloy.

mation is something higher than those with $H_2/^{15}N_2$ mixture on a solid surface without preliminary contact with methane (cf. Tables 1~4).

The result of reactions of mixture of CH_4 or H_2 with $^{15}N_2$ carried out on steel (SUS 304) are given in Table 6 by the first series of run, which is quite similar to the case of $LaNi_5$ alloy. The flash desorption carried out after these runs of reaction shows that the solid surface was covered with higher hydrocarbon and nitrogen compounds, similarly to the case with $LaNi_5$ alloy (cf. Table 5). These results suggest the contribution of higher hydrocarbon formed from discharging CH_4 and held on the solid surface to the high selectivity for hydrazine formation. This supposition was proved by the runs of reaction carried out on the same steel sample preliminarily coated with paraffin wax, as given in Table 6[12] by the second series of run. We see that the hydrogen driven out from wax by bombardment with discharging nitrogen was used for the formation of hydrazine, but not ammonia. The total pressure increased due to evolution of hydrogen gas and lower hydrocarbon, and some coking of the surfaces of steel and quartz wall of reaction vessel was observed.

Similar results were obtained at temperature as high as 100°C with reduced product of Sumatran petroleum mounted in the reaction vessel with quartz pieces. In this case, evolution of hydrogen and lower hydrocarbons

TABLE 5. $^{15}N_2$-hydrogenation with CH_4 and H_2 on $LaNi_5$ alloy.

Reactant	Gas	Trapped product			
	$-\frac{\Delta p}{\Delta t}\left(\frac{Pa}{s}\right)$	$\frac{\Delta n}{\Delta t}\left(10^2\frac{Pa\cdot cm^3}{min}\right)$	$^{15}NH_3$ (mol %)	$^{15}N_2H_4$ (mol %)	CH_4 $^{15}N_2$ (mol %)
$^{15}N_2$	0.01	(11.15)	10	87	3
			(CO_2, C_2, C_3)		
$CH_4/^{15}N_2$ 1.10	0.11	17.91	0	100	0
			(C_2', C_2~C_6)		
$H_2/^{15}N_2$ 1.10	0.12	5.40	80	20	0
$H_2/CH_4/^{15}N_2$ 0.70/1.52	0.11	21.33	21	79	0
			(C_2H_6)		
$H_2/^{15}N_2$ 3.97	0.14	7.71	66	34	0
Trapped gas by 600°C FD		(19.65)	34	66	0
			(C_3~C_6)		

TABLE 6. N_2-hydrogenation on steel SUS304.

Gas		Product			
$H_2/^{15}N_2$	$CH_4/^{15}N_2$	$\frac{dn}{dt}\left(10^2 \frac{Pa \cdot cm^3}{min}\right)$	$^{15}NH_3$	$^{15}N_2H_4$	CH_4 $^{15}N_2$
$^{15}N_2$ alone		(3.52)	0	94	3
2.76	0	12.98	90	10	0
0	1.14	41.68	0	100	0
1.15	0	13.71	59	41	0
0.95	0.81	18.18	35	65	0
1.91	0	13.53	100	0	0
2.60	0.60	19.86	50	41	0
Wax-coated steel (SUS304)					
1.01→1.71	0	(11.57)	23	77	0
0 →1.09	0	(8.85)	0	100	0

was slight, resulting in a steady formation of hydrazine and decrease of total pressure. On the other hand, ammonia was formed steadily from plasma of $H_2/^{15}N_2$ mixture on the same solid, as expected from the simple wall effect of solid surface.

Monosilane, the electronic isostar of methane, was examined as a hydrogen source and the results are given in Table 7. The time courses of runs in this Table are given in Fig. 5. The first run of reaction with $SiH_4/^{15}N_2$ mixture on quartz pieces was carried out with trap T_1 cooled at $-78°C$, so as to keep monosilane of *ca.* 5×10^2 Pa in gas phase. Monosilane was easily decomposed, resulting in the evolution of hydrogen gas and yellow-brown colored deposite on the wall. Simultaneous $^{15}N_2$-hydrogenation in this

TABLE 7. $^{15}N_2$-hydrogenation with SiH_4 and H_2 on quartz pieces.

run No.	Gas		Trapped product		
	Initial	Final	Amount (10^2 Pa·cm^3)	$^{15}NH_3$ (Mol %)	$^{15}N_2H_4$ (Mol %)
1	$\frac{SiH_4}{^{15}N_2}=1.14$	$\frac{H_2}{^{15}N_2}=1.66$	2.93	43	57
2	$\frac{^{15}N_2}{H_2}=1.72$	$\frac{H_2}{^{15}N_2}=1.43$	16.44	97	3
3	$^{15}N_2$ alone		3.51	80	20

run was slight. A similar result was obtained with $SiH_4/^{15}N_2$ mixture flowing out through the reaction vessel and trap T_1 at $-195°C$. The run 2 with $H_2/^{15}N_2$ mixture and trap T_1 at $-195°C$ showed a steady and selective formation of ammonia, as a result of the simple wall effect on the plasma of $H_2/^{15}N_2$ mixture. After the treatment of quartz surface with discharging monosilane, the run 3 carried with $^{15}N_2$ alone and trap T_1 at $-195°C$ was not steady and resulted in the preferential formation of hydrazine. In consequence, monosilane is not favorable as a hydrogen source for hydrazine synthesis on account of its high facility of decomposition in plasma to give hydrogen gas. Eventhough hydrazine was preferentially formed by the interaction of excited nitrogen molecules with deposited silicon hydride film, the notable formation of ammonia shows that the reactivity of hydrogen held in this film resembles to that of hydrogen held in $LaNi_5$ alloy rather than the higher hydrocarbons held on solid surface.

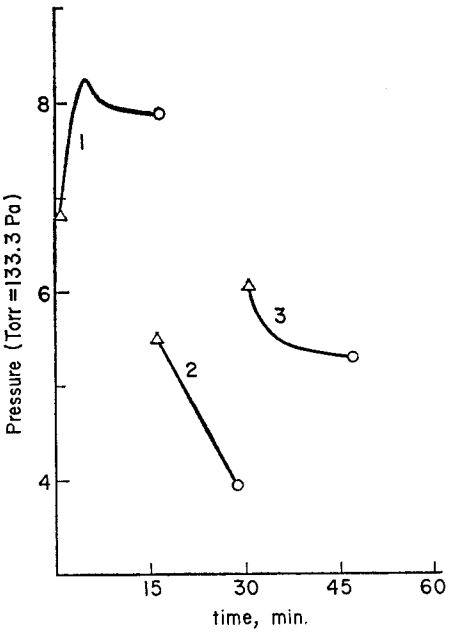


Fig. 5. Time courses of $^{15}N_2$-hydrogenation with SiH_4 and H_2 on quartz pieces.

Hydrazine is synthesize practically from ammonia by chemical process with oxidative reagent, *e.g.* NaOCl, however, ammonia was found useless in the present method as follows. At first, with respect to the report[11] on the formation of prussic acid from discharging mixture of ammonia with hydrocarbon, the reaction of $CH_4/^{15}N_2$ mixture was carried out on steel (SUS 304) by changing the cold trap T_1 from liquid nitrogen to dry ice. Methyl and ethyl cianides, presumably prussic acid as well, were found by amounts comparable with those of hydrazine and hydrocarbon. The formation of prussic acid was not clear with $^{15}N_2$ because of peaks due to $HC^{15}N$ in the mass spectra overlap with those of hydrocarbon and CO *etc.* It was ascertained by the reaction with $^{14}N_2$, with which a remarkable growth of the peak at $m/e=27$ was observed. This fact indicates that CN compounds is effectively formed by the reaction of hydrocarbon with a trace of ammonia, which were not trapped off at $-78°C$.

Figure 6 and Table 8 show the time courses of reactions of ammonia carried out on steel. After the three runs, a, b, and c, of reaction with trap T_1 at $-195°C$, the run d of ammonia alone was carried out with trap T_1 cooled at $-78°C$. Ammonia was decomposed under discharge stoichiometrically into $^{14}N_2$ and H_2, resulting in the doubled increase of the total pressure ($P/P_0=2.02$). The main part of the trapped product of slight amount was ammonia and prussic acid. In the successive run e with $H_2/^{14}N_2$ mixture,

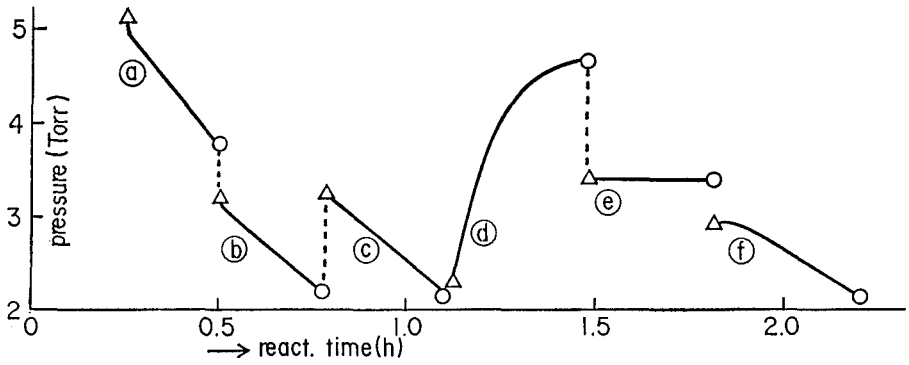


Fig. 6. Time courses of the runs of reaction given in Table 8.

TABLE 8. Effect of NH_3 on N_2-hydrogenation over stell (SUS 304).

Run no	Trap temp. (°C)	Gas: Initial	→	Gas: Final	Trapped product: Amount (10^4 Pa·cm^3)	NH_3	N_2H_4	CH_4N_2 (%)
a	−195	CH_4 / $^{15}N_2$ −1.87	→	H_2 / $^{15}N_2$ =1.97	4.282	0	100	0
b	−195	H_2 / $^{15}N_2$ −1.97	→	1.79	1.276	77	23	0
c	−195	H_2 / $^{15}N_2$ −1.79, CH_4 / $^{15}N_2$ =1.89	→	H_2 / $^{15}N_2$ −9.6	2.566	30	70	0
d	−78	$^{14}NH_3$	→	H_2 / $^{14}N_2$ =3.15, $\left(\frac{P}{P_0}=2.02\right)$	0.288	—	—	—
e	−78	H_2 / $^{14}N_2$ =3.15	→	3.44	0.076	—	—	—
f	−195	CH_4 / $^{15}N_2$ =1.26	→	H_2 / $^{15}N_2$ =1.39	2.053	26	74	0
g	−195	600°C FD			0.293	54	46	0

reaction was practically absent. The run f with $CH_4/^{15}N_2$ mixture and trap T_1 at $-195°C$ showed an evident induction period at the early stage of the reaction. In comparison with the result of the run a, the remarkable formation of ammonia in the run f is suggestive for the hydrogenation of nitrogen held on the solid surface in the preceding runs, d and e, with H_2/NH_3 mixture. It is well known that iron is easily converted to its nitride by carring out decomposition of ammonia on it, but not by the treatment with nitrogen or its mixture with hydrogen.[16] Furthermore, taking account of that the N_2-hydrogenation should occur by the interaction of plasma with the quartz wall of reaction vessel before the contact of plasma with steel surface, the apparent inactivity shown by runs e and f in Fig. 6 indicates the high catalytic activity of the metal surface coated with its nitride for decomposition of the nitrogen compounds. The nitride film may be hydrogenated off as ammonia in the early stage of the run f, and, afterwards, a usual activity for hydrazine formation from $CH_4/^{15}N_2$ mixture may be recovered.

(C) *Reaction scheme*

The results of the present experiments are summerized in the scheme given in Fig. 7. In conclusion, the hydrazine synthesis from N_2 gas over solid surface was performed by applying glow discharge to gas and trapping off the formed nitrogen compounds immediately after the contact of plasma with solid surface. The effect of glow discharge for hydrazine formation might mainly based on the formation of excited nitrogen molecules (presumably, $A^3\Sigma u^+$ state with long life), which collide with OH groups or hydrocarbon on the solid surface to driving out excited H atoms, presumably proton and/or radical. The bombarding N_2 molecule and the excited H atoms are quenched as hydrazine molecule by the wall effect of the solid surface.

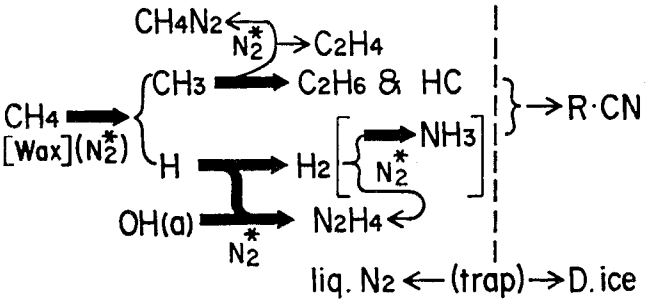


Fig. 7. Reaction scheme of N_2-hydrogenation on solid surface with various hydrogen sources under glow discharge.

Hydrogen gas is poorly effective for hydrazine formation due to its difficulty for the supplement of OH groups onto the solid surface and preferentially forms ammonia due to the simple wall effect of solid surface on the plasma of H_2/N_2 mixture. The selective formation of hydrazine from CH_4/N_2 mixture presumably based on the interaction of excited N_2 molecules with higher hydrocarbon formed on the solid surface from discharging methane. It should be noted that water vapor was poison for the present N_2-hydrogenation.

The contributions of homogeneous reaction possibly taking place in plasma and the catalytic activity of solid surface are not clear for the present.

Results of the present experiments are expected to bring light on the field of plasma chemistry, especially with respect to the wall effect and/or the catalytic action of the solid surfaces and the reactivity of excited nitrogen molecule.

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