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N_2-HYDROGENATION ON SOLID SURFACE WITH GLOW DISCHARGE

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The steady and selective N_2-hydrogenation to hydrazine on solid surface was performed at room temperature by the use of glow discharge of N_2 gas over higher hydrocarbon film held on solid surface. Formation of ammonia from H_2/N_2 mixture was found to be due to the simple wall effect of solid surface on the plasma.

The direct synthesis of hydrazine on metal oxide surface under glow discharge was previously concluded$^{1)}$ to be caused by the protonation of excited N_2 molecule with OH groups chemisorbed on the metal oxide surface, which is called as surface-OH in what follows. This conclusion was further ascertained by the present experiment, at first. The apparatus and experimental procedure were the same as the previous one,$^{1)}$ except the position of the strain gauge, P_s, which was attached to the trap T_1, as shown in Fig. 1, to measure the amount of trapped product. The reaction on (100) single crystallites of MgO (from Tateho Chem. Co. Ltd.) was repeated, as well as the successive flash desorption (FD) up to 600 °C for 10 min. We see by the parenthesized figures in Table 1 that the amount (10^2Pa·cm^3) of trapped product of the 10 min reaction with N_2 alone, which was N_2H_4 nearly all, decreased by this repetition of runs. The trapped product from H_2/N_2 mixture also became poor in N_2H_4 content. This result might be due to the decrease of the amount of surface-OH. This supposition was proved by the reaction on MgO crystallites preliminarily treated with KOH aqueous solution and evacuated at 600 °C, with which the ion exchange of surface-OH to form

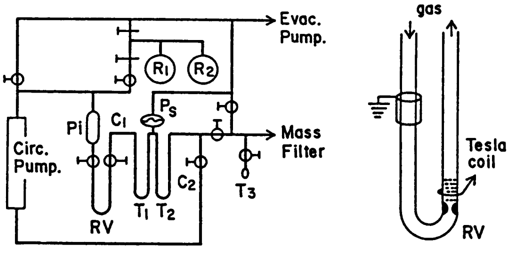

Fig.1. Scheme of reaction apparatus.

Table 1. Reproducibility of $^{15}N_2$-hydrogenation on MgO(100) single crystallites

Solid	Gas		Product			
	$H_2/^{15}N_2$ ratio	$-\Delta P/\Delta t$ (Pa/s)	$\Delta n/\Delta t$ ($10^2 \frac{Pa\cdot cm^3}{min}$)	$^{15}NH_3$:$^{15}N_2H_4$:$CH_4{}^{15}N_2$ (Mol %)		
MgO	N_2 alone	0.0	(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
	N_2 alone	0.0	(0.35)	13	81	4
	0.60	0.11	6.57	92	3	5
	600 °C FD		(0.61)	40	60	0
	N_2 alone	0.0	(0.29)	7	88	5
	0.92	0.12	7.57	97	2	1
	600 °C FD		(0.44)	50	50	0
K/MgO	N_2 alone	0.0	0.03	0	75	25
	1.63	0.35	——	100	0	0
K/MgO (H_2O, 500 °C)	N_2 alone	0.0	0.03	22	78	0
	0.72	0.19	——	100	0	0

Table 2. $^{15}N_2$-hydrogenation on $LaNi_5$(0.9 g) at room temperature

Pre-treatment	Gas		Product			
	$H_2/^{15}N_2$	$-\frac{\Delta p}{\Delta t}(\frac{Pa}{s})$	$\frac{\Delta n}{\Delta t}(10^2\frac{Pa\cdot cm^3}{min})$	$^{15}NH_3$;$^{15}N_2H_4$:CH_4 $^{15}N_2$ (Mol %)		
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

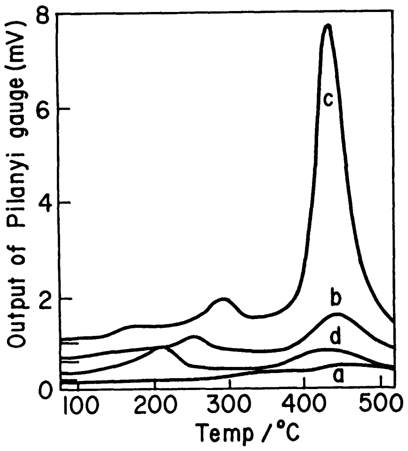

Fig. 2. Flash desorption spectra of $LaNi_5$ given in Table 2.

surface-OK is expected.[2)] We see in Table 1 that the product from $H_2/^{15}N_2$ mixture was solely ammonia, indicating that the surface-OH was eliminated and the dissociation of excited N_2 molecule may be promoted by surface potassium as reported for the ammonia synthesis over iron catalyst.[3)]

The previous result[1)] that the reaction of $H_2/^{15}N_2$ mixture were independent of the sort of metal oxide suggests that the reaction was mainly caused by the wall effect of metal oxide surface on the plasma of $H_2/^{15}N_2$ mixture. If so, similar results will be obtained with solid surfaces other than metal oxide. The reaction was carried out on various metals, *e.g.* , Pt, Ni, Fe, stainless steel(SUS304), Si, Zr, a-$Ti_{30}Ni_{66}$, a-$Pd_{0.35}Zr_{0.65}H_{1.0}$ and $LaNi_5$ alloy in the form of tips, and metal sulfides, *e.g.* , MoS_2 single crystallites and CoS powder. These samples were preliminarily evacuated at 600 °C for 10 min or more. After being cooled at room temperature, glow discharge was applied to circulating $^{15}N_2$ or its mixture with H_2. The results were quite similar to those on quartz pieces and MgO crystallites,[1)] as illustrated in Table 2 by the first or the third series of the reactions carried out on $LaNi_5$ alloy. The parenthesized figures in this Table give the total amount (10^2Pa·cm^3) of trapped product of *ca.* 10 min reaction. Such a unique result obtained with $H_2/^{15}N_2$ mixture irrespective of the sort of solid surface proves the simple wall effect of the solid on the discharging gas.

Relating to the reactivity of hydrogen from different sources, the $^{15}N_2$-hydrogenation with hydrogen dissolved in $LaNi_5$ alloy and that of methane was examined. Figure 2 shows the flash desorption spectra of the alloy treated as given in Table 2. The desorbed gas at temperatures below 350 °C was nitrogen compounds and that above 350 °C was solely hydrogen. We see from curves b) and d) that hydrogen was absorbed by the alloy during the reaction with $H_2/^{15}N_2$ mixture even at room temperature. Hydrogen was charged to the alloy, evacuated at 600 °C, by the discharge of hydrogen gas alone at room temperature. The hydrogen pressure was decreased from 7×10^3 Pa to 10 Pa by this discharge. The $^{15}N_2$-hydrogenation was carried out after evacuation at room temperature. We see in Table 2 that, under

Table 3. $^{15}N_2$-hydrogenation with CH_4 and H_2 on $LaNi_5$ alloy

Gas		Product			
Reactant	$-\frac{\Delta p}{\Delta t}(\frac{Pa}{s})$	$\frac{\Delta n}{\Delta t}(10^2\frac{Pa\cdot cm^3}{min})$	$^{15}NH_3$:$^{15}N_2H_4$:$CH_4{}^{15}N_2$ (Mol %)		
$^{15}N_2$	0.01	(11.15)	10	87	3
$CH_4/^{15}N_2$ 1.10	0.11	17.91	0 (HC: C_2', $C_2\sim C_6$)	100	0
$H_2/^{15}N_2$ 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 (C_2H_6)	79	0
$H_2/^{15}N_2$ 3.97	0.14	7.71	66	34	0
Trapped gas by 600 °C FD		(19.65)	34 (HC: $C_3\sim C_6$)	66	0

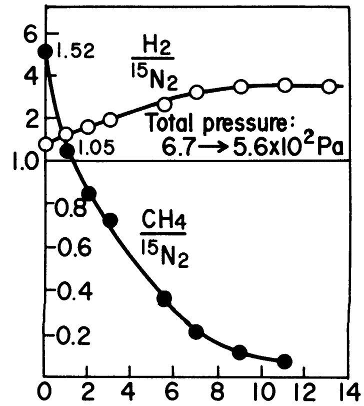

Fig. 3. Reaction of $^{15}N_2$ with CH_4 on $LaNi_5$ alloy.

Table 4. $^{15}N_2$-hydrogenation on stainless steel(SUS304)

Gas		Product			
$H_2/^{15}N_2$ ratio	$CH_4/^{15}N_2$ ratio	$\Delta n/\Delta t$ $(10^2\frac{Pa\cdot cm^3}{min})$	$^{15}NH_3$:$^{15}N_2H_4$:$CH_4{}^{15}N_2$ (Mol %)		
$^{15}N_2$ alone		(3.52)	0	94	3
2.76	0.0	12.89	90	10	0
0	1.14	41.68	0	100	0
1.15	0.0	13.71	59	41	0
0.95	0.84	18.18	35	65	0
Paraffin wax coated steel					
$^{15}N_2$ alone →1.09	0.0	(8.85)	0	100	0
1.09 →1.71	0.0	(11.57)	23	77	0

the discharge of $^{15}N_2$ alone, ammonia was formed considerably as compared with the same reaction on the alloy preliminarily evacuated at 600 °C. This result indicates the hydrogen diffused onto the surface of the alloy being used preferentially for the formation of ammonia.

The course of reaction of $^{15}N_2$ with CH_4 at 6.7×10^2 Pa total pressure is shown in Fig. 3. Methane dissociated to give hydrogen gas and C_2- and/or higher hydrocarbon and, simultaneously, $^{15}N_2$ was hydrogenated selectively into hydrazine, as seen in Table 3. A quite similar result was obtained with stainless steel(SUS304) as given in Table 4, where we see, furthermore, that the selectivity for hydrazine formation is still higher in the reaction of $H_2/^{15}N_2$ mixture carried our just after the reaction of $^{15}N_2$ with CH_4. This result suggests the contribution of higher hydrocarbon formed on the metal surface during the preceding reaction with CH_4. This supposition was proved with the same steel sample coated with paraffin wax. As given in Table 4, the hydrogen driven out from wax by bombardment with discharging nitrogen was used for the formation of hydrazine, but not ammonia. Hydrogen gas and lower hydrocarbons were evolved simultaneously and some coking of the surfaces of steel and quartz of the reaction vessel was observed.

With respect to the report[4)] on the formation of prussic acid from discharging mixture of hydrocarbon with ammonia, the reaction of CH_4/N_2 mixture was carried out by changing the cold trap T_1 from liquid nitrogen to dry ice. Methyl and ethyl

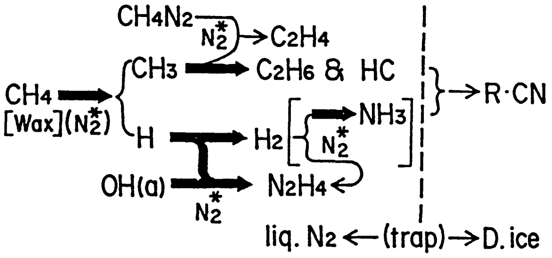

Fig. 4. The reaction scheme of N_2-hydrogenation with hydrogen and/or its compounds on solid surface under silent discharge of gas.

cianides, at least, were found by amounts comparable with those of hydrazine and hydrocarbon. This fact indicates that CN compounds were effectively formed by the reaction of hydrocarbon with ammonia, which was not completely trapped off at -78 °C.

The results of the present experiments are summerized in the reaction scheme given in Fig. 4. 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 molecule, which collides with OH groups or hydrocarbon on the solid surface to driving out excited H atoms, presumably proton and/or radical, and is quenched as hydrazine molecule by the wall effect of the solid. So far as hydrazine synthesis concerned, hydrogen gas is poorly effective due to its difficulty for the surface-OH supplement. 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 action of solid surface are not clear for the present. The selective formation of hydrazine from CH_4/N_2 mixture presumably based on the interaction of excited N_2 molecule with higher hydrocarbon formed on the solid surface from discharging methane. Further investigation is in progress and will be reported elsewhere.

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