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THE RATE-DETERMINING STEP OF AMMONIA DECOMPOSITION OVER A WELL-REDUCED DOUBLY PROMOTED IRON CATALYST

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Abstract

The rate of ammonia decomposition over a well-reduced doubly promoted iron catalyst was followed in a flow system using a bench scale reactor. The rate V was found to depend on partial pressures P_A and P_H of ammonia and hydrogen as,

$$V = k_1(P_A/P_H^{1.5})^{\alpha} \quad \text{about } 420°\text{C},$$

$$V = k_2(P_A/P_H^{0.5})^{\beta} \quad \text{above } 479°\text{C},$$

where constants k_1, k_2, α and β depended sensitively on the experimental conditions. At or above 517°C, the rate was depressed by nitrogen slightly but perceptibly, whereas not at all at a lower temperature. It is inferred from these results that the rate-determining step of ammonia decomposition changes with rise of reaction temperature from the desorption of nitrogen adatoms to one of the steps of dehydrogenation of ammonia on catalyst surface.

Introduction

Catalyzed decomposition of ammonia over iron catalysts has been extensively studied in connection with the synthesis. It has prevailingly been accepted that the rate-determining step of the reaction was desorption of nitrogen adatoms[1)2)3)]. The rate equation proposed by TEMKIN and PYZHEV[4)] based on this mechanism has so far satisfactorily accounted for the experimental results.

The works performed by ENOMOTO and HORIUTI and ENOMOTO, HORIUTI and KOBAYASHI[5)] threw doubt upon the mechanism that the rate-determining step was the desorption of nitrogen adatoms. They determined the stoichiometric number of the rate-determining step to be two with reference to the overall reaction $N_2 + 3H_2 = 2NH_3$, from which it followed that one of hydrogenation steps was rate-determining, insofar as the overall reaction proceeded through the sequence of steps

$$N_2 \longrightarrow 2N(a) \qquad (1)$$

$$H_2 \longrightarrow 2H(a) \qquad (2)$$

$$N(a) + H(a) \longrightarrow NH(a) \qquad (3)$$

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$$NH(a)+H(a) \longrightarrow NH_2(a) \qquad (4)$$
$$NH_2(a)+H(a) \longrightarrow NH_3 \qquad (5)$$

HORIUTI and one of the present authors[6], subsequently concluded that the step (3) was rate-determining, in accordance with the observation of stoichiometric number, by the statistical mechanical analysis of the kinetics of the decomposition in a flow system at one atmospheric pressure. BOKHOVEN, GORGELS and MARS[7] have later determined the stoichiometric number of the rate-determining step to be one in accordance with the generally accepted view but their determination was numerically so sensitive to the equilibrium pressure of ammonia that it varied from one to two within errors of their observation of the equilibrium pressure[8]. Recently TANAKA, YAMAMOTO and MATSUYAMA[9] determined the stoichiometric number to be one below 430°C by a new method. TAMARU[10] conducted the adsorption measurments in course of the reaction and suggested on the basis of the results that the rate-determining step switched over from step (1) to one of the hydrogenation step (3), (4) or (5) with rise of reaction temperature or decrease of partial pressure of hydrogen.

The present work is devoted to discriminate between these conflicting views on the mechanism of ammonia decomposition with special reference to the promoter distribution and surface structure of the catalyst; the latter specificities of catalyst might depend on the preparation of catalyst, especially the reduction procedure as inferred from the prononced effect of promoters on the kinetics and the activity as found by LOVE and EMMETT[11] and by LOVE and BRUNAUER[12].

Experimentals

Mixtures of ammonia, hydrogen, nitrogen or/and helium were led over the catalyst kept at a required temperature at a total pressures of 1 atm. Partial pressures of ammonia, hydrogen and nitrogen were varied by varying the mixing ratio keeping the total inflow rate constant in order to secure a constant contact time for a small extent of decomposition using helium as a means of dilution. The apparatus is shown schematically in Fig. 1. The ammonia outflow rate was determined by backtitrating sulfuric acid solution, in which ammonia had been absorbed, with sodium hydroxide solution of a known concentration. The steady state of decomposition was confirmed by a constant outflow rate of ammonia. Inflow rate of each gas was measured by a capillary flow meter.

Commercially available gases in cylinders were used after the following treatments. Ammonia was dried over soda lime (Apparent vol.: 400 cc) and over fused potassium hydroxide (Apparent vol.: 800 cc). Both helium and nitrogen were purified by passing them separately through the chambers containing nickel turnings at 450°C, a first tower containing silica gel (Apparent vol.: 400 cc), chambers containing copper gauze kept at 450°C, a second tower containing silica gel and then, after being mixed, through reduced iron catalyst at 500°C.

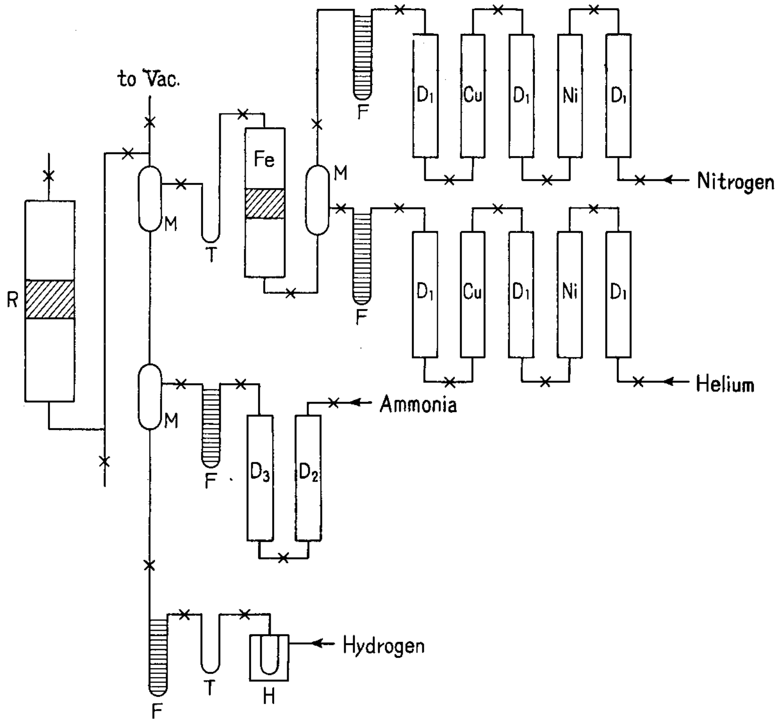

Fig. 1. Apparatus for Ammonia Decomposition. D_1 *etc.*; drying towers; D_1, silica gel; D_2, soda lime; D_3, potassium hydroxyde. F, flow meter. H, hydrogen purifier (Pd-Ag thimble). Ni, Cu, Fe, converters packed with nickel, copper and iron. R, reaction chamber. T, trap. M, bulb for mixing gas components.

Hydrogen was diffused through a thimble of palladium-silver alloy and passed through a trap immersed in liquid nitrogen.

Fused ammonia-syntetic iron catalyst used contained 4.72% of alumina, 0.31 % of potassium oxide and 0.05% of silica as promoters. The catalyst was of 12 to 14 mesh size and of apparent volume of 3.5 cc/10 g, the bed length of catalyst being about 2 cm. It was reduced in a stream of hydrogen at a flow rate of 500 cc STP/min. The weight of catalyst before reduction and its reduction schedules are summarized in Table I. The temperature of the catalyst was measured by an alumel-chromel thermocouple which has been calibrated by the standard method.

The experiments were conducted by allowing ammonia and hydrogen, mixed with either or both of nitrogen and helium, to flow over the well-reduced catalyst at 1 atm. total pressure and at temperature ranging from 390 to 560°C. The partial pressure of ammonia at the inlet of catalyst bed ranged from 0.25 to 0.88 and that of nitrogen from 0 to 0.49 atm.

One and the same sample of catalyst was repeatedly used being reduced before each series and subject to different treatments inbetween. Experiments of Series I to V were thus conducted with catalyst each after the reduction of schedule specified in Table I. The catalyst

TABLE I. Specification of Catalyst

Series of Experiment	Weight of Catalyst before Reduction (g)	Reduction Schedules	
I	10	450°C	for 45 hrs.
II		550	94
III		600	94
VI*)		450	45
VII		600	62
IX**)	2	600	21

*) Catalyst was that used for Series V not listed in the Table, intentionally oxidized in air at 450°C for 45 hrs. and then reduced.

**) Catalyst was a portion of that used in preceeding series.

was poisoned with water vapor in course of Series IV, and the catalyst was treated with ammonia of 1 atm. pressure to form nitride prior to Series V***). The catalyst was now oxidized before Series VI in air for 45 hrs. at 450°C and then reduced at 450°C for 45 hrs. in order to investigate the effect for oxidation-reduction treatment of catalyst upon reaction rate and kinetics. Series subsequent to VI were performed without oxidation similarly to Series I, II and III except that in Series IX a portion of the catalyst used in the foregoing series was employed or the poisoning with water vapor was repeated in course of Series VIII.***)

Results

The results are shown in Fig. 2 to 11****) and in Tables II and III. The decomposition rate of ammonia was observed by varying the inflow rates N_A, N_H and N_N respectively of ammonia, hydrogen and nitrogen with the total inflow rate N_T kept constant using purified helium as diluent. The partial pressures P_A, P_H and P_N respectively of ammonia, hydrogen and nitrogen at the inlet of catalyst bed were calculated by multiplying the total pressure of 1 atm. by the ratio of inflow rate of the respective gas to N_T.

Table III shows the surface area and promoter distribution on the catalyst surface, as determined by the usual method[13]; V_m is the volume of monolayer adsorption of nitrogen as determined by the BET method at $-195°C$ and V_{CO} or V_{CO_2} is that of chemisorbed carbon monoxide or carbon dioxide respectively[13]. The percent of Fe, K_2O or Al_2O_3 and/or SiO_2 as given in the Table is that of V_{CO}, V_{CO_2} or $V_m - V_{CO} - V_{CO_2}$ on V_m.

Fig. 2 to 11 show the logarithm of the amount of decomposition of ammonia $(N_A - n_A)$ versus $\log P_A$ or $\log P_H$, where n_A is the outflow rate of

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***) To be published

****) Results are also tabulated in Appendix I.

TABLE II. Effect of Nitrogen on the Rate of Decomposition

Series	Temp. °C	P_A atm.	P_H atm.	P_N atm.	NH_3 decomposed ($N_A - n_A$) cc STP/min
I	390	0.109	0.411	0	5.1
	390	0.109	0.411	0.480	5.8
	423	0.115	0.450	0.435	27.3
	423	0.115	0.450	0	27.5
II	424	0.1118	0.448	0	14.4
	424	0.1112	0.447	0.422	14.3
	469	0.110	0.457	0	58.9
	469	0.110	0.452	0.438	58.3
	469	0.0193	0.456	0	16.3
	469	0.0189	0.446	0.480	15.3
III	424	0.113	0.445	0	14.7
	424	0.113	0.442	0.445	15.4
	469	0.112	0.445	0	46.4
	469	0.1139	0.445	0.441	45.4
	517	0.0877	0.575	0.337	87.1
	517	0.0877	0.575	0	91.4
	517	0.0877	0.575	0.321	85.3
	517	0.0877	0.575	0.237	87.7
	517	0.0877	0.575	0	90.9
IX	479	0.0916	0.618	0	16.2
	479	0.0914	0.618	0.290	15.7
	551	0.0914	0.618	0.290	51.8
	551	0.0916	0.619	0	54.6

TABLE III. Surface Area and Promoter Distribution

Reduction Schedule	Quantity*) adsorbed cc STP/10 gm catalyst			Fe	K_2O	Al_2O_3 and/or SiO_2
	V_m	V_{CO}	V_{CO_2}	%	%	%
450°C for 37 hrs.	41.2 (18.1)	7.9	11.0	19.2	26.7	55.1
550 88	33.7 (14.8)	6.2	9.6	18.4	28.5	53.1
600 67	27.4 (12.0)	4.95	8.0	18.0	29.2	52.8

*) V_m: Volume of monolayer adsorption of nitrogen by BET-method; figures in bracket show the surface areas m^2/g.
V_{CO}, V_{CO_2}: Volume of chemisorbed CO or CO_2.

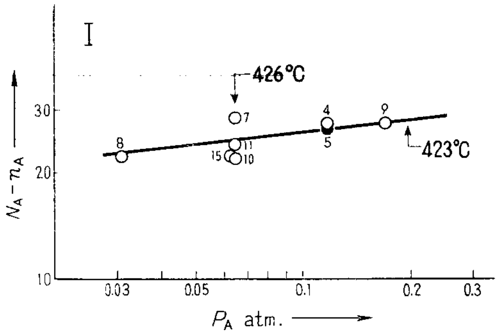

Fig. 1. Amount of ammonia decomposed ($N_A - n_A$) *vs.* partial pressure P_A of ammonia. N_A, inflow rate of ammonia; n_A, outflow rate of ammonia. Total inflow, 890 cc STP/min; Hydrogen inflow, 400 cc STP/min. Numbers in Figure designate the number of runs. In the absence of nitrogen in gas mixture in inflow (○). In the presence of nitrogen in gas mixture in inflow (●).

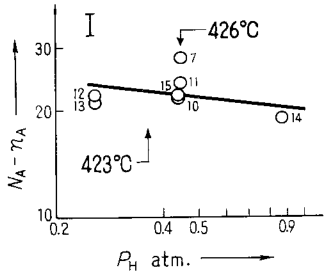

Fig. 3. Amount of ammonia decomposed ($N_A - n_A$) *vs.* partial pressure P_H of hydrogen. N_A, inflow rate of ammonia; n_A, outflow rate of ammonia. Total inflow, 890 cc STP/min; Ammonia inflow, 58.4 cc STP/min. Numbers in Figure designate the number of runs. In the absence of nitrogen in gas mixture in inflow (○).

ammonia; ($N_A - n_A$) gives the amount of decomposition in a definite contact time with catalyst, assured by the constant total inflow rate for a small extent of decomposition. The slope of curves gives order x or y of the reaction with respect to ammonia or hydrogen in the latter case, Table IV shows the values x and y thus obtained at different temperatures. Both x and $-y$ increased from Series I to II, while runs of Series I are closely reproducible as seen in Figs. 2 and 3, which may be attributed to the reduction of catalyst at 550°C after Series I. The x and y varied, however, no more appreciable by reduction at 600°C repeated prior to Series III as seen in Table IV. Appreciable change of x and y was neither observed after the poisoning with water vapor in Series IV, the nitride formation prior to Series V,*) oxidation-reduction treatment of catalyst prior Series VI and the further reduction at 600°C prior to Series VII. Along with rise of reaction temperature from *ca.* 420 to *ca.* 480°C in Series IX, x increased, while $-y$ decreased, so that $-y/x$ was reduced to one-thirds. It may be noted that the promoter distribution was practically independent of the reduction schedules, although the surface area decreased with rise of reduction temperature.

As shown in Table II the effect of nitrogen on the decomposition rate is imperceptible at or below 479°C, whereas the rate is slightly but perceptibly

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*) To be published

TABLE IV. The experimental Values of x and y*)

Series	Temp. °C	x	$-y$	$-y/x$
I	423	0.08	0.13	1.62
II	424	0.48	0.75	1.56
III	424 432	0.43 —	— 0.64	— —
VI	423 427	0.41 —	— 0.57	— —
VII	423	0.41	—	—
IX	479 488	0.73 0.81	0.30 —	0.41 —

*) See Appendix II. and also Table in the Appendix.

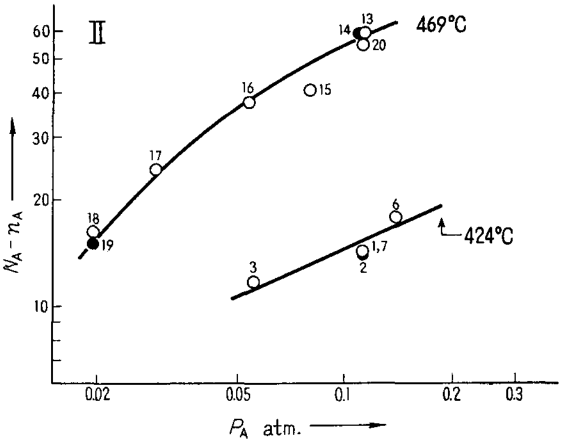

Fig. 4. Amount of ammonia decomposed ($N_A - n_A$) *vs.* partial pressure P_A of ammonia. N_A, inflow rate of ammonia; n_A, outflow rate of ammonia. Total inflow, 890 cc STP/min (424°C); Hydrogen inflow, 398 cc STP/min (424°C). Total inflow, 900 cc STP/min (469°C); Hydrogen inflow, 413 cc STP/min (469°C). Number in Figure designate the number of runs. In the absence of nitrogen in gas mixture in inflow (○). In the presence of nitrogen in gas mixture in inflow (●).

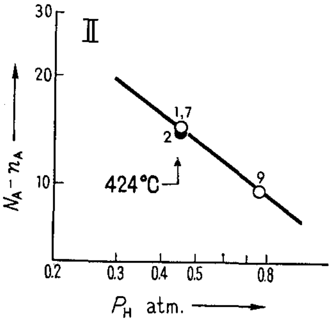

Fig. 5. Amount of ammonia decomposed ($N_A - n_A$) *vs.* partial pressure P_H of hydrogen. N_A, inflow rate of ammonia; n_A, outflow rate of ammonia. Total inflow, 890 cc STP/min; Ammonia inflow, 99.2 cc STP/min. Number in Figure designate the number of runs. In the absence of nitrogen in gas mixture in inflow (○). In the presence of nitrogen in gas mixture in inflow (●).

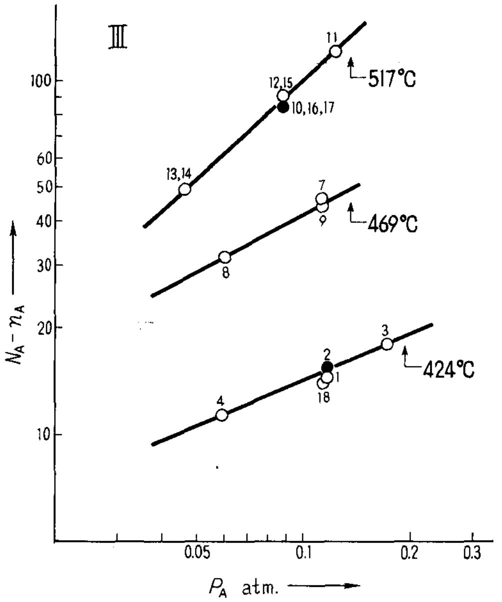

Fig. 6. Amount of ammonia decomposed ($N_A - n_A$) *vs.* partial pressure P_A of ammonia. N_A, inflow rate of ammonia; n_A, outflow rate of ammonia. Total inflow, 890 cc STP/min (424 and 469°C); Hydrogen inflow, 398 cc STP/min (424 and 469°C). Total inflow inflow, 1150 cc STP/min (517°C); Hydrogen inflow, 662 cc STP/min (517°C). Number in Figure designate the number of runs. In the absence of nitrogen in gas mixture in inflow (○). In the presence of nitrogen in gas mixture in inflow (●).

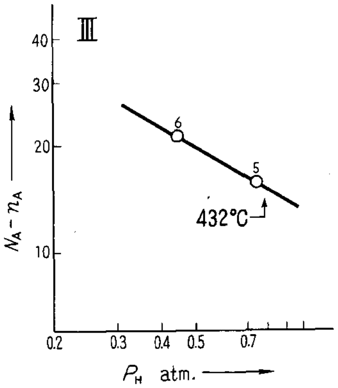

Fig. 7. Amount of ammonia decomposed ($N_A - n_A$) *vs.* partial pressure P_H of hydrogen. N_A, inflow rate of ammonia; n_A, outflow rate of ammonia. Total inflow, 890 cc STP/min; Ammonia inflow, 101 cc STP/min. Number in Figure designate the number of runs. In the absence of nitrogen in gas mixture in inflow (○).

depressed in its presence outside the experimental errors*) at 517 and 551°C.

Discussion

A number of works have been contributed to the catalyzed synthesis and decomposition of ammonia in the presence of doubly and singly or pure iron catalyst. The TEMKIN-PYZHEV equation

$$V = k(P_A/P_H^{1.5})^{\alpha} \tag{6}$$

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*) Errors of determination of the amount of ammonia decomposed were kept within ± 0.5 cc STP.

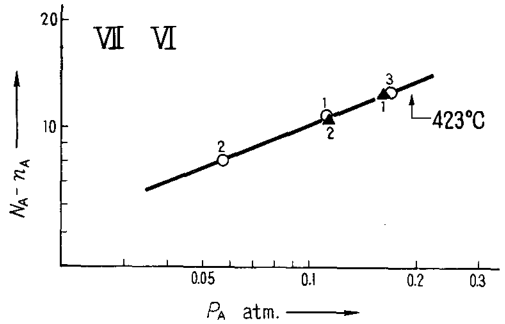

Fig. 8. Amount of ammonia decomposed ($N_A - n_A$) *vs.* partial pressure P_A of ammonia. N_A, inflow rate of ammonia; n_A, outflow rate of ammonia. Total inflow, 890 cc STP/min; Hydrogen inflow, 398 cc STP/min. Numbers in Figure designate the number of runs. In the absence of nitrogen in gas mixture in inflow (○ Series VI, ▲ Series VII).

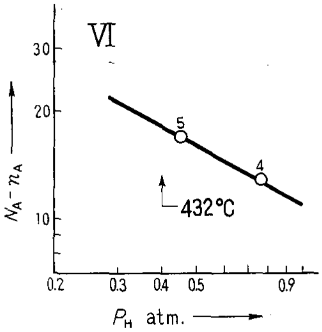

Fig. 9. Amount of ammonia decomposed ($N_A - n_A$) *vs.* partial pressure P_H of hydrogen. N_A, inflow rate of ammonia; n_A, outflow rate of ammonia. Total inflow, 890 cc STP/min; Ammonia inflow, 98.9 cc STP/min. Numbers in Figure designate the number of runs. In the absence of nitrogen in gas mixture in inflow (○).

is accepted as providing a satisfactory description of kinetics both of the synthesis and decomposition, which was derived from the assumption that the rate was determined by adsorption or desorption of nitrogen.

As mentioned with reference to Table IV, the decomposition rate of Series II follows Eq. (6) for $\alpha \fallingdotseq 0.5$, whereas $\alpha \fallingdotseq 0.1$ in Series I which has never been observed before in the presence of doubly promoted iron catalysts. It should be noted that the results are quite similar to that obtained by Love and EMMETT[11] on a singly promoted iron catalyst under some conditions. Neither a correlation is found between the low value of α of Series I and the promoter distribution, which is much the same as in other Series as seen from Table II. LOVE and EMMETT[11] have found that the rate of decomposition on doubly promoted iron catalyst (931) was proportional to $P_A^{0.6}/P_H^{0.85}$ or $\alpha = 0.6$ which is close to our results apart from the different content of promoters in the catalyst. and that the rate was proportional to $P_H^{1.2}/P_A^{0.8}$ on a singly promoted iron catalyst at temperature from 400 to 425°C. SCHWAB and KRABETZ[14] have found that α was equal to 1 on non-promoted iron catalyst at 370°C.

The kinetics of decomposition observed at 479°C in Series IX is apparently different from those obtained around 420°C in respect that $-y/x$ is as seen in Table IV close to 0.5 instead of 1.5 in accordance with the TEMKIN-PYZHEV equation. It is, besides, remarkable that nitrogen inhibits the decomposition at

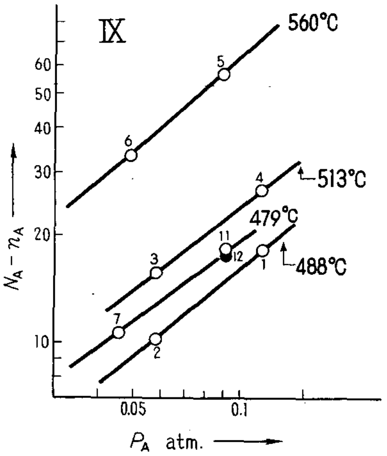

Fig. 10. Amount of ammonia decomposed $(N_A - n_A)$ *vs.* partial pressure P_A of hydrogen. N_A, inflow rate of ammonia; n_A, outflow rate of ammonia. Total inflow, 890 cc STP/min (488 and 513°C); Hydrogen inflow, 668 cc STP/min (488 and 513°C). Total inflow, 1090 cc STP/min (479 and 560°C); Hydrogen inflow, 668 cc STP/min (479 and 560°C). Numbers in Figure designate the number of runs. In the absence of nitrogen in gas mixture in inflow (○). In the presence of nitrogen in gas mixture in inflow (●).

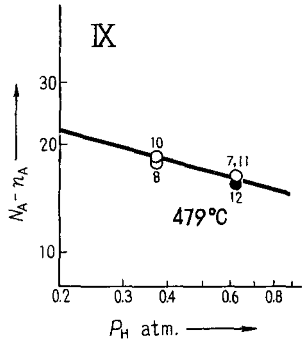

Fig. 11. Amount of ammonia decomposed $(N_{;} - N_A)$ *vs.* partial pressure P_H of hydrogen. N_A, inflow rate of ammonia; n_A, outflow rate of ammonia. Total inflow, 1090 cc STP/min; Ammonia inflow, 99 cc STP/min. Numbers in Figure designate the number of runs. In the absence of nitrogen in gas mixture in inflow (○). In the presence of nitrogen in gas mixture in inflow (●).

517 and 551°C, although slightly but perceptibly. It follows that the desorption of nitrogen adatoms can not be the rate-determining step of decomposition under the latter experimental conditions, where the reverse rate is practically ignorable*). Nitrogen may in consequence be in partial equilibrium with nitrogen adatoms, which retard the reaction. The present experimental results under the latter condition contradicts the kinetics that the decomposition rate be proportional to $(P_A/P_H)^{\alpha}/P_H$ as expected from the rate equation of NH_3 synthesis which was derived by OZAKI, TAYLOR and BOUDART[15) from the assumption that the adsorption of nitrogen is rate-determining step and the surface is covered with NH(a).

In the previous experiments which were performed by HORIUTI and one of the present authors[6), the rate of decomposition in the presence of doubly

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*) The backward rate amounts to be *ca.* 6.9×10^{-3} times the forward rate at 517°C as shown in Appendix III.

promoted iron catalyst could be reproduced over the temperature range between 450 and 532°C by the equation

$$V = k(P_A/P_H) \Big/ \left\{1 + a(P_N)^{1/2}\right\}^2 \qquad (7)$$

as derived from the assumption of the rate-determining step of $NH(a) \rightarrow N(a) + H(a)$, retarded by N(a) in equilibrium with gaseous nitrogen, where constant k and a have been statistical-mechanically evaluated to confirm the observed values. The latter result as to nitrogen effect is qualitatively in conformity with the present result obtained above 517°C but not quantitatively, which is not accounted for at the moment. It is to be noted that the activity of the present catalyst is a hundred times higher than that used by them[6].

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Appendix I

Experimental Results for Ammonia Decomposition over Doubly Promoted Catalyst

Series	Number of runs	Temp, °C	Inflow rate of ammonia N_A cc STP/min	Inflow rate of hydrogen N_H cc STP/min	Inflow rate of nitrogen N_N cc STP/min	Inflow rate of helium N_{He} cc STP/min	Total inflow rate N_T cc STP/min	Outflow rate of ammonia n_A cc STP/min	Ammonia decomposed N_A-n_A cc STP/min
I	1	390	103	382	413	0	898	97.9	5.1
	2	390	101	380	0	446	927	95.2	5.8
	3	390	48.9	190	0	223	462	44.2	4.7
	4	423	99.2	400	391	0	890	71.9	27.3
	5	423	99.2	400	0	392	891	71.7	27.5
	6	423	58.8	228	0	222	509	31.6	27.2
	7	426	58.4	400	0	435	893	29.9	28.5
	8	423	28.0	400	0	465	893	5.77	22.23
	9	423	154	400	0	342	896	126.5	27.5
	10	423	58.4	400	0	440	898.4	36.7	21.7
	11	423	58.4	400	0	435	893.4	34.2	24.2
	12	423	58.4	227	0	592	877	36.7	21.7
	13	423	58.4	227	0	605	890.4	37.5	20.9
	14	423	58.4	802	0	62	922.4	39.3	19.1
	15	423	58.4	400	0	442	900	36.5	21.9

II	1	424	99.2	398	0	390	887.2	84.8	14.4
	2	424	99.2	398	390	0	890.2	84.9	14.3
	3	424	49.8	398	0	450	897.8	38.3	11.5
	6	424	127	398	0	378	904.0	109.4	17.6
	7	424	99.2	398	0	390	887.2	84.7	14.5
	9	424	99.5	663	0	115	877.5	90.0	9.5
	10	424	117.4	300	0	500	917.4	102.0	15.4
	12	424	117.4	300	0	500	917.4	100.4	17.0
	11	454	117.4	300	0	500	917.4	77.3	40.1
	13	469	100.2	413	0	391	904	41.3	58.9
	14	469	100.2	413	401	0	914	41.9	58.3
	15	469	70.6	413	0	398	884	29.7	40.5
	16	469	47.8	413	0	435	895.8	10.6	37.2
	17	469	26.7	413	0	470	910	2.47	24.2
	18	469	17.5	413	0	475	905.5	1.17	16.33
	19	469	17.5	413	445	50	925.5	2.17	15.33
	20	469	102.2	413	0	385	900.2	47.7	54.5
III	1	424	101	398	0	396	895	86.3	14.7
	2	424	101.7	398	400	0	899.7	86.3	15.4
	3	424	155.2	398	0	348	901.2	137.4	17.8
	4	424	51.4	398	0	435	884.4	40.0	11.4
	18	424	101	398	0	396	895	87.0	14.0
	5	432	101	662	0	127	890	85.3	15.7
	6	432	101	398	0	396	895	78.9	21.1

Series	Number of runs	Temp. °C	Inflow rate of ammonia N_A cc STP/min	Inflow rate of hydrogen N_H cc STP/min	Inflow rate of nitrogen N_N cc STP/min	Inflow rate of helium N_{He} cc STP/min	Total inflow rate N_T cc STP/min	Outflow rate of ammonia n_A cc STP/min	Ammonia decomposed N_A-n_A cc STP/min
III	7	469	100.3	398	0	396	894.3	53.9	46.4
	8	469	52.5	398	0	435	885	20.6	31.9
	9	469	101.6	398	395	0	894.6	56.2	45.4
	10	517	101	662	389	0	1152	13.91	87.1
	11	517	146	662	0	390	1198	23.1	122.9
	12	517	101	662	0	390	1153	9.6	91.4
	13	517	52	662	0	435	1149	2.25	49.75
	14	517	53.2	662	0	435	1150.2	4.37	48.9
	15	517	101	662	0	390	1153	10.09	90.9
	16	517	101	662	380	0	1152	15.73	85.3
	17	517	101	662	272	112	1147	13.3	87.7
VI	1	423	99.1	398	0	398	896	88.4	10.7
	2	423	50.4	398	0	442	890.4	42.4	8.0
	3	423	148.4	398	0	342	888.4	136.3	12.1
	4	427	98.9	657	0	112	867.9	86.0	12.9
	5	427	98.9	398	0	398	895	82.1	16.8
VII	1	423	147.3	398	0	356	901	135.0	12.3
	2	423	98.8	398	0	397	894	88.4	10.4

IX	1	488	99	668	0	112	889	81	18
	2	488	49.6	668	0	135	874.4	39.4	10.2
	3	513	49.6	668	0	135	874.4	33.8	15.8
	4	513	99	668	0	112	889	72.3	26.7
	5	560	99	668	0	348	1115	42.1	56.9
	6	560	49.6	668	0	300	1017.6	15.7	33.9
	7	479	99	668	0	314	1081	82.8	16.2
	8	479	99	413	0	585	1097	81	18.0
	9	479	49.6	413	0	635	1097.6	38.9	10.7
	10	479	99	413	0	585	1097	80.8	18.2
	11	479	99	668	0	314	1081	82.8	16.2
	12	479	99	668	316	0	1083	83.3	15.7
	13	551	99	668	316	0	1083	47.2	51.8
	14	551	99	668	0	314	1081	44.4	54.6

Appendix II

Determination of Constants in Rate Equation allowed for the Variation of Partial Pressures.

Allowance has been made by simplifying the rate equation $V=kP_A^x/P_H^y$ as $V=k(P_A/P_H^{1.5})^\alpha$ for observations around 420°C or as $V=k(P_A/P_H^{0.5})^\beta$ for those at and above 479°C.

HORIUTI and one of the present authors[6)] have derived an equation of the steady rate of decomposition V in cc S.T.P./min cc catalyst in flow system that

$$\int_{x_e^A}^{x_0^A} \frac{1}{(1+x^A)^2} \frac{dx^A}{V} = \frac{v}{N_T+N_A} \tag{i}$$

from the postulates of piston flow and homogeneous temperature in the catalyst bed, where x_0^A, x_e^A or x^A represents the mol fraction of ammonia at the inlet, exit or at any horizontal section of the catalyst bed and v is the apparent volume of catalyst.

The simplified rate equation is written in terms of total pressure P and mol fractions x^A and x^H of ammonia and hydrogen according to the relations $P_A=Px^A$ and $P_H=Px^H$ as

$$V=k_1\left\{x^A/P^{0.5}(x^H)^{1.5}\right\}^\alpha, \tag{ii. a}$$

or

$$V=k_2\left\{x^A P^{0.5}/(x^H)^{0.5}\right\}^\beta. \tag{ii. b}$$

Substituting V from (ii. a) or (ii. b) into (i), we have

$$K_1=\frac{1}{P^{0.5\alpha}}k_1=\left(\frac{N_T+N_A}{v}\right)\int_{x_e^A}^{x_0^A}(x^H)^{1.5\alpha}\Big/(1+x^A)^2(x^A)^\alpha\cdot dx^A, \tag{iii. a}$$

or

$$K_2=P^{0.5\beta}k_2=\left(\frac{N_T+N_A}{v}\right)\int_{x_e^A}^{x_0^A}(x^H)^{0.5\beta}\Big/(1+x^A)^2(x^A)^\beta\cdot dx^A, \tag{iii. b}$$

where K_1 and K_2 are constants. We have on the other hand from stoichiometry of the decomposition, on the basis of the postulate of piston flow

$$\frac{N_A-n_A}{2}=\frac{n_H-N_H}{3} \tag{iv}$$

where n_A *etc.* are the flow rates of ammonia *etc.* respectively across the horizontal section of the catalyst bed. The mol fraction x^A, x^H, x_0^A or the value x_0^H at the inlet of x^H is expressed in terms of the latter quantities as

$$x^{\mathrm{A}} = n_{\mathrm{A}} \big/ (N_{\mathrm{T}} + N_{\mathrm{A}} - n_{\mathrm{A}}) \,, \quad x^{\mathrm{H}} = n_{\mathrm{H}} \big/ (N_{\mathrm{T}} + N_{\mathrm{A}} - n_{\mathrm{A}}) \,, \qquad \text{(v. A), (v. H)}$$

$$x_0^{\mathrm{A}} = N_{\mathrm{A}} \big/ N_{\mathrm{T}} \quad \text{or} \quad x_0^{\mathrm{H}} = N_{\mathrm{H}} \big/ N_{\mathrm{T}} \,. \qquad \text{(vi. A), (vi. H)}$$

We have now eliminating $N_{\mathrm{A}}/N_{\mathrm{T}}$, $N_{\mathrm{H}}/N_{\mathrm{T}}$, $n_{\mathrm{A}}/N_{\mathrm{T}}$, and $n_{\mathrm{H}}/N_{\mathrm{T}}$ from (iv), (v. A), (v. H), (vi. A) and (vi. H),

$$x^{\mathrm{H}} = \frac{\{3(x_0^{\mathrm{A}} - x^{\mathrm{A}}) + 2x_0^{\mathrm{H}}(1 + x^{\mathrm{A}})\}}{2(1 + x_0^{\mathrm{A}})} \,. \qquad \text{(vii)}$$

Subsituting x^{H} from (vii) into (iii. a) or (iii. b), we have

$$K_1 = \frac{N_{\mathrm{T}} + N_{\mathrm{A}}}{v} \int_{x_{\mathrm{e}}^{\mathrm{A}}}^{x_0^{\mathrm{A}}} \frac{\left\{ \dfrac{3(x_0^{\mathrm{A}} - x^{\mathrm{A}}) + 2x_0^{\mathrm{H}}(1 + x^{\mathrm{A}})}{2(1 + x_0^{\mathrm{A}})} \right\}^{1.5\alpha}}{(1 + x^{\mathrm{A}})^2 (x^{\mathrm{A}})^{\alpha}} dx^{\mathrm{A}} \qquad \text{(viii. a)}$$

or

$$K_2 = \frac{N_{\mathrm{T}} + N_{\mathrm{A}}}{v} \int_{x_{\mathrm{e}}^{\mathrm{A}}}^{x_0^{\mathrm{A}}} \frac{\left\{ \dfrac{3(x_0^{\mathrm{A}} - x^{\mathrm{A}}) + 2x_0^{\mathrm{A}}(1 + x^{\mathrm{A}})}{2(1 + x_0^{\mathrm{A}})} \right\}^{0.5\beta}}{(1 + x^{\mathrm{A}})^2 (x^{\mathrm{A}})^{\beta}} dx^{\mathrm{A}} \,. \qquad \text{(viii. b)}$$

K_1 or K_2 was now calculated by (viii. a) or (viii. b) for trial value of α or β ranging from 0 to 1.5 on the basis of the values of x_0^{A}, $x_{\mathrm{e}}^{\mathrm{A}}$, x_0^{H} and $(N_{\mathrm{T}} + N_{\mathrm{A}})/v$ determined by the experiments at different constant temperatures. The value of α or β was thus determined to be of the value given in the following Table which minimizes the fluctuation of K_1 or K_2. The α or β value thus obtained was found in close agreement with x-value in Table IV as it should be for a small extent of decomposition.

Constants in Rate Equation allowed for the Variation of partial Pressures.

Series	Temp. °C	α	β	K_1 $\frac{\text{cc S.T.P.}}{\text{cc cat. min}}$	K_2 $\frac{\text{cc S.T.P.}}{\text{cc cat. min}}$
I	423	0.08	—	8.0 ± 0.84	—
II	424	0.43	—	6.6 ± 0.1	—
III	424	0.40	—	6.6 ± 0.1	—
	432	0.49	—	10.8	—
IX	517	—	0.73	—	243 ± 7.6
	479	—	0.74	—	118 ± 1.67
	488	—	0.81	—	147
	513	—	0.72	—	190
	560	—	0.60	—	357

Appendix III

Evaluation of the Backward Rreaction Rate of Ammonia Decomposition.

The observed rate V is expressed[6) as

$$V = V_{+} - V_{-} = V_{+}\left[1 - \left(\frac{P_{\mathrm{N}} P_{\mathrm{H}}^{3}}{K_{\mathrm{P}} P_{\mathrm{A}}^{2}}\right)^{1/\nu_r}\right]$$

where V_{+} or V_{-} is the forward or backward rate of decomposition, ν_r the stoichiometric number of the rate-determining step and K_{P} the equilibrium constant of reaction $2NH_3 = N_2 + 3H_2$. The second term in the parenthesis is now evaluated according to the empirical equation of HABER*)

$$-\frac{1}{2}\log_{10} K_{\mathrm{p}} = \frac{9591}{4.571\,T} - \frac{4.98}{1.985}\log_{10} T$$
$$- \frac{4.6 \times 10^{-4}}{4.571} T + \frac{8.5 \times 10^{-7}}{4.571} T^{2} + 2.10$$

with reference to the present experimental condition. The result was that the second term was 6.3×10^{-3} at most for $\nu_r = 1$ in accordance with the rate-determining step in question in the text. The backward rate is hence practically negligible.

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*) F. HABER, Z. Elektrochem. **20**, 603 (1914).