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MECHANISM OF CATALYZED DECOMPOSITION OF AMMONIA IN THE PRESENCE OF DOUBLY PROMOTED SYNTHETIC CATALYST.

III: Hysteresis of the Decomposition Rate

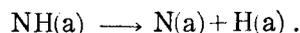
By

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(Received September 15, 1958)

Introduction

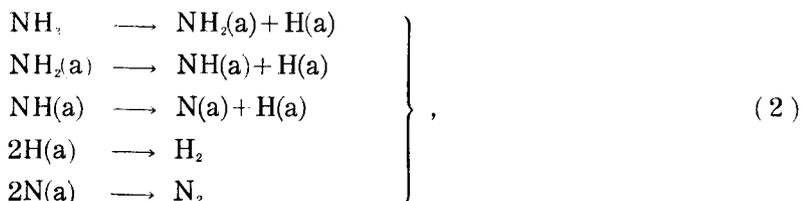
It has been shown in the foregoing paper¹⁾ that the catalyzed decomposition of ammonia in the presence of doubly promoted synthetic catalyst is governed by the dissociation of adsorbed imino group NH(a) into adsorbed nitrogen atom N(a) and hydrogen atom H(a), i. e.



This conclusion has been arrived at by analyzing the following experimental result²⁾ according to the generalized theory of reaction rate^{3,4)} on the basis of the previous conclusion of ENOMOTO, HORIUTI and KOBAYASHI⁵⁾ that the stoichiometric number of the rate-determining step of the catalyzed ammonia synthesis or decomposition



is 2, which confines the part of determining the rate to the first three steps of the sequence



where (a) signifies the adsorbed state. Ammonia-hydrogen mixture of 1:4 mol ratio was allowed to flow²⁾ at different definite rates through a bed of the catalyst under the atmospheric pressure at 450°-540°C to

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observe the outflow rate of ammonia until a steady value was attained at each definite inflow rate, and the decomposition rate of ammonia per unit quantity of the catalyst was determined from the result correcting for the effect of the deviation from the piston flow and the temperature homogeneity in the catalyst's bed.

It is well-known on the other hand that iron forms various iron nitrides⁶⁾⁻¹²⁾ depending on the temperature and the composition of gas around it. Observations of the ammonia decomposition over the synthetic catalyst¹³⁾⁻¹⁴⁾ have hitherto been carried out at the α -phase state of the catalyst inclusive of the foregoing works¹⁾⁻²⁾ of the present authors. KOBAYASHI and NISHIZIMA¹⁵⁾ have observed the decomposition of ammonia in ammonia-hydrogen mixtures of various compositions over a few different samples of ammonia synthetic catalysts from 380° to 535°C and found that the decomposition rate was unstable and varied hysteretically with composition of gas at the transition from α - to γ' - or from γ' - to ϵ -phase of nitrides.

It has now been found by experiments similar to the previous one²⁾ that the steady outflow rate of ammonia, finally attained at definite inflow rate and composition of inflow gas, revealed a quite stable and reproducible hysteresis at 1 atm total pressure and 487°C, as the inflow rate of hydrogen was increased stepwise from one to another constant value and then decreased similarly at a fixed inflow rate of ammonia, and this result has been accounted for as described below on the basis of the mechanism of decomposition concluded in the foregoing paper¹⁾ and the known phase equilibrium of iron-nitrogen system.

§ 1. Experimental

The present experiments have been carried out in continuation to the foregoing experiment²⁾ using the same apparatus with the same catalyst's bed.

After the previous experiment²⁾, an observation of the hysteresis similar to that described below was preliminarily conducted and then the catalyst bed was flown with pure ammonia at 70 cc min⁻¹ flow rate at 475°C for 48 hours. The reaction chamber filled with ammonia was now cooled down to room temperature and left standing for ten months. Pure hydrogen was now allowed to flow over the catalyst at 200 cc min⁻¹ rate at 550°C for 48 hours, then cooled down to 487°C and the gas flow was switched to that of 1 : 4 ammonia-hydrogen mixture to conduct a run just in the same way as in the foregoing experiment²⁾.

Having thus kept check with activity of the catalyst, the catalyst was now subjected to the preliminary treatment described in the

foregoing paper²⁾, i. e. flowing it with pure hydrogen at 550°C for 4 to 5 hours and then the present observation of the hysteresis was started by lowering the temperature of the catalyst to 487°C and by switching the gas flow to that of ammonia-hydrogen mixture of specified composition. Each run of a definite composition of inflow gas was continued for 4 to 100 hours until the outflow rate N'_A of ammonia remained perfectly constant, when the inflow gas was switched to other composition by increasing or decreasing inflow rate N_H of hydrogen fixing that N_A of ammonia at 70 cc min⁻¹ throughout.

The percent R of ammonia decomposition, i. e. $R \equiv 100(N_A - N'_A)/N_A$ at the latter steady state finally attained for each constant composition of the inflow gas is given in Table 1 and plotted against the ratio N_H/N_A as shown in Fig. 1. Numbers of runs annexed to points in the figure show the order of them having been carried out.

These points lie, as shown in Fig. 1, reproducibly on a single curve BAA' which descends monotonously with increase of N_H/N_A , so far as the runs were started at N_H/N_A greater than 4 and then conducted at

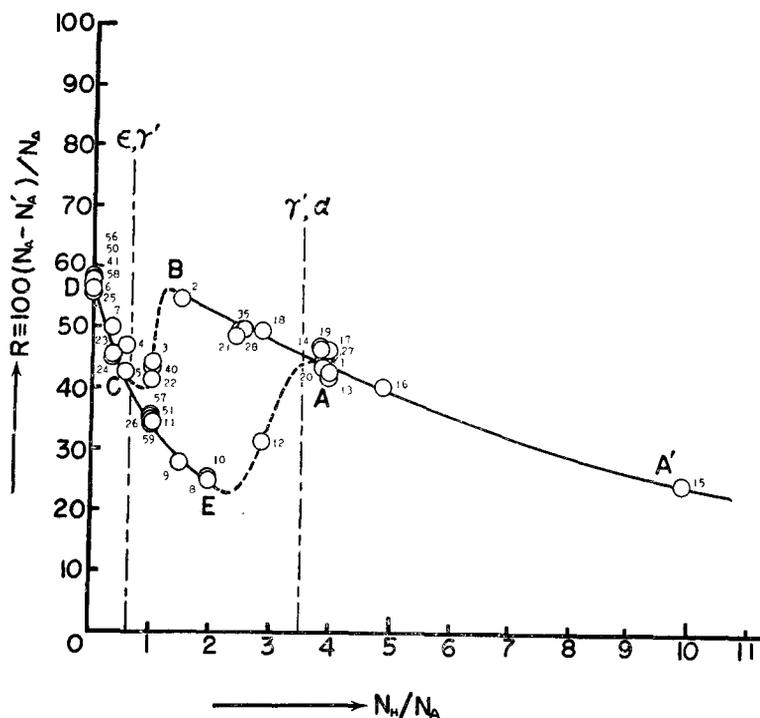


Fig. 1. Hysteresis of percent R of ammonia decomposition.
487°C, $N_A = 70$ cc NTP min⁻¹.

Mechanism of Catalyzed Decomposition of Ammonia III

TABLE 1. Hysteresis of ammonia decomposition

Inflow rate N_A of NH_3 : 3.125×10^{-3} mol $\text{min}^{-1} = 70.0$ cc NTP min^{-1}

No. of runs	Date	Temperature ^{*)} °C					Inflow rate N_H of H_2 mol $\text{min}^{-1} \times 10^3$	$\frac{N_H}{N_A}$	Outflow rate N_A of NH_3 mol $\text{min}^{-1} \times 10^3$	Percent decomposition of NH_3 $R = 100 \frac{N_A - N_A'}{N_A}$
		t_1	t_2	t_3	t_4	Average				
1	1953 Dec. 10	484	484	484	496	487	12.41	3.97	1.793	42.6
2	11	484	484	484	496	487	4.656	1.49	1.414	54.8
3	16	484	484	486	496	488	3.156	1.01	1.745	44.2
4	17	484	484	486	496	488	1.788	0.57	1.659	46.9
5	18	484	484	481	496	486	1.788	0.57	1.794	42.6
6	19	484	484	481	496	486	0	0	1.370	56.2
7	19	484	484	481	496	486	0.981	0.31	1.563	50.0
8	19	484	484	486	496	488	6.125	1.96	2.344	25.0
9	19	484	484	486	496	488	4.656	1.49	2.257	27.8
10	21	484	484	484	496	487	6.125	1.96	2.331	25.4
11	22	484	484	484	496	487	3.156	1.01	2.047	34.5
12	22	484	484	484	496	487	2.149	2.86	2.149	31.2
13	24	484	484	484	496	487	12.41	3.97	1.817	41.9
14	27	484	484	484	496	487	11.97	3.83	1.676	46.6
15	28	484	481	486	501	488	28.75	9.92	2.500	20.0
16	28	484	484	484	496	487	15.23	4.89	1.363	40.4
17	29	484	484	484	496	487	12.41	3.97	1.680	46.3
18	29	484	484	484	496	487	8.938	2.86	1.580	49.4
19	30	484	484	484	496	487	11.97	3.83	1.661	46.9
20	1954 March 16	484	486	481	496	487	12.13	3.88	1.766	43.5
21	17	484	484	481	496	487	7.500	2.40	1.603	48.6
22	20	486	484	481	496	487	3.056	0.98	1.828	41.5
23	26	486	484	481	496	487	1.228	0.39	1.702	45.6
24	26	486	484	481	496	487	1.228	0.39	1.717	45.1
25	27	486	484	481	496	487	0	0	1.387	55.6
26	27	486	484	484	496	487	3.056	0.98	2.037	34.8
27	27	486	484	481	496	487	12.14	3.88	1.725	44.8
28	June 16	486	484	484	496	488	7.946	2.54	1.573	49.7
35	21	486	484	481	496	487	7.725	2.47	1.585	49.3
40	July 6	486	484	481	496	487	3.125	1.00	1.765	43.5
41	7	484	484	484	496	487	0	0	1.316	57.9
50	13	484	484	484	496	487	0	0	1.313	58.0
51	13	484	484	484	496	487	3.059	0.98	2.080	35.4
56	29	484	484	484	496	487	0	0	1.305	58.2
57	30	484	484	484	496	487	3.059	0.98	2.016	35.5
58	Aug. 1	484	484	484	496	487	0	0	1.339	57.2
59	2	484	484	484	496	487	3.059	0.98	2.050	34.4

*) The t_1 , t_2 , t_3 , and t_4 are temperatures read by thermojunctions inserted at different positions in the catalyst's bed of 54.5 cc total volume packed in a vertical quartz cylinder, gas mixture being passed through it from the top to the bottom; t_1 , t_2 and t_3 are readings of thermojunctions on the axis of the bed, respectively at the top, middle and bottom, and t_4 is that on the wall at the middle. Cf. Ref. 2.

N_H/N_A kept above 1.5 throughout. As N_H/N_A was decreased below 1.5 at the point 3, the percent of ammonia decomposition continued to decrease for a long time down to a constant value appreciably lower than R of the foregoing runs at higher N_H/N_A ; it took 67 hours for the point 3 to attain its final value R plotted in Fig. 1 which was then kept constant for further 30 hours as far as observed. Decreasing N_H/N_A further, R rose now as shown in the Figure up to the point D, where $N_H/N_A=0$. Increasing N_H/N_A now reversely, former points on the curve DC were reproduced as far as *ca.* $N_H/N_A=0.5$ at C, but beyond that R traced another curve CE lying below CBA. Points were now reproducibly on the single curve DCE descending monotonously with increasing N_H/N_A so long as N_H/N_A did not exceed 2. As it did, the R increased above the point E as with the point 12, and with increase of N_H/N_A , R restored the former value on BAA' thus completing the hysteresis.

It was found in the observation of the point 12 that the outflow rate of ammonia initially exceeded its inflow rate. This excess outflow of ammonia decreased rapidly to vanish within first 20 minutes of the observation, its R being attained after 16 hours and kept for further

TABLE 2. Percent decomposition of ammonia
at $N_H/N_A = 2.5$

No. of runs	Date	Temperature**) °C					Inflow rate of		Outflow rate N'_A of NH_3 $\text{mol min}^{-1} \times 10^3$	Percent decomposition of NH_3 $R \equiv 100 \frac{N_A - N'_A}{N_A}$
		t_1	t_2	t_3	t_4	Average	Ammonia N_A $\text{mol min}^{-1} \times 10^3$	Hydrogen N_H $\text{mol min}^{-1} \times 10^3$		
28*)	1954 June 16	486	484	484	496	488	3.125	7.946	1.573	49.7
29	16	486	484	484	496	488	6.652	16.67	4.939	24.8
30	17	486	484	484	496	488	0.893	2.232	0.186	79.1
31	19	486	484	484	496	488	1.116	2.768	0.296	73.4
32	20	486	484	484	496	488	1.464	3.741	0.506	65.4
33	20	486	484	484	496	488	1.786	4.464	0.692	61.2
34	21	486	484	484	496	488	2.232	5.598	1.054	52.8
35*	21	484	484	484	496	488	3.125	7.725	1.585	49.3
36	21	486	484	484	496	488	4.464	11.12	2.846	36.3
37	21	479	481	486	499	488	17.86	44.64	15.38	13.8
38	22	486	484	484	496	488	2.500	6.161	1.218	51.3
39	23	486	484	484	496	488	3.540	8.928	2.067	41.6

*) Duplicated in Table 1.

**) Cf. footnote *) to Table 1.

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TABLE 3. Percent decomposition of ammonia
at $N_H = 0$

No. of runs	Date	Temperature**) °C					Inflow rate N of NH_3 mol min ⁻¹ × 10 ³	Outflow rate N'_A of NH_3 mol min ⁻¹ × 10 ³	Percent decomposition of NH_3 $R \equiv 100 \frac{N_A - N'_A}{N_A}$
		t_1	t_2	t_3	t_4	Average			
6*)	1953 Dec. 19	484	484	481	496	486	3.125	1.370	56.2
25*)	1954 March 27	486	484	481	496	486	3.125	1.387	55.6
41*)	July 7	484	484	484	496	487	3.125	1.316	57.9
42	7	486	484	484	496	488	8.882	5.156	42.0
43	8	486	484	481	496	487	4.465	2.196	50.8
44	8	489	484	481	499	488	23.13	15.83	31.6
45	10	489	484	484	499	488	12.54	7.777	36.4
46	10	489	484	479	501	488	44.20	34.46	22.0
47	10	489	484	481	496	488	5.603	28.46	49.2
48	12	486	484	484	496	488	3.540	1.652	53.3
49	12	486	484	484	496	488	1.750	0.642	63.3
50*)	13	484	484	484	496	487	3.125	1.313	58.0
55	15	484	484	481	494	486	4.465	2.115	52.6
56*)	28	484	484	484	496	487	3.125	1.305	58.2
58*)	Aug. 2	484	484	481	496	486	3.125	1.339	57.2

*) Duplicated in Table 1. **) Cf. footnote *) to Table 1.

TABLE 4. Percent decomposition of ammonia
at $N_H/N_A = 1$

No. of runs	Date	Temperature**) °C					Inflow rate of		Outflow rate N'_A of NH_3 mol min ⁻¹ × 10 ³	Percent decomposition of NH_3 $R \equiv 100 \frac{N_A - N'_A}{N_A}$
		t_1	t_2	t_3	t_4	Average	Ammonia N_A mol min ⁻¹ × 10 ³	Hydrogen N_H mol min ⁻¹ × 10 ³		
11*)	1953 Dec. 22	484	484	484	496	487	3.125	3.170	2.047	34.5
26	1954 March 27	486	484	484	496	487	3.125	3.056	2.037	34.8
51*)	July 13	486	484	484	496	487	3.103	3.058	2.018	35.4
52	13	484	484	484	496	487	8.929	8.929	7.400	17.1
53	14	484	484	484	496	487	4.465	4.465	3.174	28.9
54	14	484	484	484	496	487	0.893	0.893	0.402	55.0
57*)	30	484	434	481	496	486	3.125	3.059	2.016	35.5

*) Duplicated in Table 1. **) Cf. footnote *) to Table 1.

12 hours as far as observed. The similar excess has been observed at the second cycle of tracing the hysteresis, when the value of $N_{\text{H}}/N_{\text{A}}$ was switched from 1 at the point 26 to 4 at the point 27.

After the above determination of the points 28, 41 and 51 respectively at $N_{\text{H}}/N_{\text{A}}$ of 2.5, 0 and 1, the inflow rate of gas mixture of constant composition was varied in each case just as in the previous work²⁾, before passing to the observation of next point. The steady values R thus determined are shown in Table 2, 3 and 4 side by side with data given in Table 1 respectively at the same $N_{\text{H}}/N_{\text{A}}$.

The reproducibility of the results is established by the Figure and these Tables. The result of the preliminary run with 1:4 mixture provides a further check of the reproducibility, as mentioned above, as compared with the run 37 in Table 1 of the foregoing paper²⁾.

§ 2 Theoretical

The hysteresis observed is now accounted for on the basis of the previous conclusions¹⁾ and the knowledge of the phase equilibria of iron-nitrogen system⁶⁾⁻¹²⁾ under the postulates (I) that the sequence (2) is followed whether the catalyst's surface is at the state of α -phase or any nitride, (II) that the rate-determining step is



on α -phase and



on any nitride, (III) that the backward rate of (4) is negligible compared with its forward rate, (IV) that the steady rate of decomposition is smaller when governed by (4) than by (3), and (V) that N(a) is in equilibrium with constituent nitrogen atom N(F) of α -phase or nitrides.

The steady rate V_s is given according to (I) and (III) with special reference to (3) and (4) as^{*})

$$V_s = k_1(a_{\text{NH}} - a_{\text{N}}a_{\text{H}}) = k_2a_{\text{N}}^2, \quad (5)$$

where a_{NH} , a_{N} and a_{H} are absolute activities of NH(a) , N(a) and H(a)

) It is admitted for the present qualitative discussion, that the activity coefficient f^ of the critical complex is constant throughout, the general expression for the rate v of a thermal step being $v = ka^l/f^*$ (cf. Ref. 4), where k is the rate constant and a^l the activity product of the relevant initial complex.

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respectively defined by the relevant chemical potential μ^{NH} etc. as

$$\mu^{\text{NH}} = RT \ln a_{\text{NH}} \text{ etc.}, \quad (6)$$

and k_1 and k_2 are rate constants of Steps (3) and (4), which are respectively common to the forward and backward rates of the appropriate step, since at equilibrium the forward and backward rates are equal to each other on the one hand, and absolute activities of the initial and final complexes are the same by the definition of (6), e. g. a_{NH} and $a_{\text{N}a_{\text{H}}}$ then equal to each other, on the other hand.

Three steps of the scheme (2) other than (3) and (4) are now practically in equilibrium respectively according to (I) and (II), so that

$$a_{\text{NH}_3} = a_{\text{NH}_2} a_{\text{H}}, \quad a_{\text{NH}_2} = a_{\text{NH}} a_{\text{H}}, \quad a_{\text{H}}^2 = a_{\text{H}_2}, \quad (7. a), (7. b), (7. c)$$

where a_{NH_2} is the absolute activity of $\text{NH}_2(a)$ and a_{NH_3} and a_{H_2} are those of ammonia and hydrogen in gas. It follows from (7)

$$a_{\text{NH}} = a_{\text{NH}_3}/a_{\text{H}_2}, \quad a_{\text{H}} = a_{\text{H}_2}^{1/2}, \quad (8. a), (8. b)$$

i. e. that a_{NH} and a_{H} are respectively fixed at a given composition of the gas mixture, which defines a_{NH_3} and a_{H_2} . If now (4) determines the rate according to (II), so that (3) is kept in equilibrium, we have further

$$a_{\text{NH}} = a_{\text{N}} a_{\text{H}}$$

or according to (8)

$$a_{\text{N}} = a_{\text{NH}_3}/a_{\text{H}_2}^{3/2} \quad (9. a)$$

In the case of the rate-determining step of (3), when $a_{\text{N}} a_{\text{H}}$ is definitely smaller than a_{NH} , we have

$$a_{\text{N}} < a_{\text{NH}_3}/a_{\text{H}_2}^{3/2} \quad (9. b)$$

instead. Eq. (9) states that $a_{\text{NH}_3}/a_{\text{H}_2}^{3/2}$ is the upper limit to a_{N} in general and is approached by a_{N} particularly as (4) controls the rate, or in other words, that a_{N} depends not only on the composition of the gas mixture around, which defines $a_{\text{NH}_3}/a_{\text{H}_2}^{3/2}$, but also on the history of the catalyst's surface which decides the rate-determining step by (II). The a_{N} , thus determined kinetically by the surface state of the catalyst, reciprocally conditions the latter, giving rise to the stable hysteresis as illustrated in what follows.

§ 3 Phase Equilibria

Fig. 2 reproduces the experimental results of EMMETT and col-

laborators^{6,7}), PARANJPE and collaborators¹¹) and BURDESE¹²) by the plot of the ammonia percent in ammonia-hydrogen mixture at 1 atm total pressure, which is in equilibrium with the solid phase formed from pure iron and the same gas mixture, against the nitrogen content in the solid phase in weight percent of nitrogen or in the corresponding atomic ratio of nitrogen to iron. The height of the horizontal line gives the composition of the gas mixture at the equilibrium of the reaction



i. e. at that of α -phase (Fe) and γ' -phase (Fe_4N) or that at the similar equilibrium of γ' - and ϵ -phase. The ammonia percent at the equilibrium of (10) is interpolated from the observation of the equilibrium constant $P_{\text{H}_2}^{3/2}/P_{\text{NH}_3}$ by EMMETT^{6,7}) or LEHRER⁹) respectively at 22.4 or 21.8%

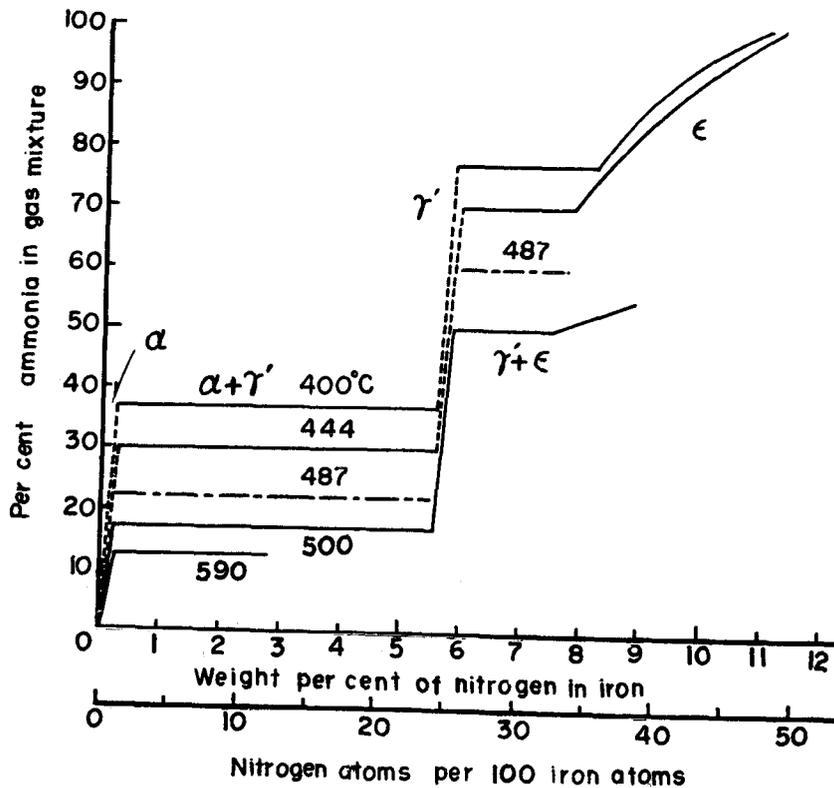


Fig. 2. Phase diagram of iron-nitrogen system quoted from Refs. 7 (400°C, 444°C), 11 (500°C), and 12 (590°C) or interpolated (487°C) from the data given in Refs. 6, 7 and 9.

for the temperature 487°C of the present observation, while that of the γ', ϵ -equilibrium similarly from the observation by EMMETT^(6,7) or LEHRER⁽⁹⁾ respectively at 60.2 or 59.5%, where P_{H_2} or P_{NH_3} is the partial pressure of hydrogen or ammonia at the equilibrium.

The vertical chain line signified by γ', α or ϵ, γ' in Fig. 1 indicates the value $(N_H/N_A)_0$ or $(N_H/N_A)'$ of N_H/N_A , respectively appropriate to the mean value of the above pair of the ammonia percents at the γ', α - or ϵ, γ' -equilibrium. It is seen from the Figure that the hysteresis in question begins to appear, just as N_H/N_A passes $(N_H/N_A)_0$ from above to below, i. e. the stable phase changes from α to γ' .

§ 4 Explanation of Hysteresis

We consider first α - and γ' -phase only, assuming as if γ' -phase were the only nitride. At the equilibrium of (10) in particular, when α -phase coexists with γ' -phase, we have according to (V) another equilibrium of the reaction



so that the particular value $a_{N,0}$ of a_N at the equilibrium of (11) is determined as^{*})

$$a_{N,0} = (a_{NH_3}/a_{H_2}^{3/2})_0, \quad (12)$$

where suffix 0 signifies the particular value at the equilibrium of (10), i. e. that at the point $N_H/N_A = (N_H/N_A)_0$. It follows from the phase equilibrium of (11) that the α - or γ' -phase is stable respectively according as a_N is lower or higher than $a_{N,0}$.

Consider now the catalyst at the entrance of the bed, which is flown steadily with the inflow gas. The $a_{NH_3}/a_{H_2}^{3/2}$ of the inflow gas increases monotonously with decrease of N_H/N_A , because of the proportionality of a_{NH_3} to N_A and that of a_{H_2} to N_H , equaling $a_{N,0}$ by (12), when $N_H/N_A = (N_H/N_A)_0$. If (4) governs the rate, a_N equals $a_{NH_3}/a_{H_2}^{3/2}$ according to (9.a) and hence increases with decrease of N_H/N_A , coinciding with $a_{N,0}$, when $N_H/N_A = (N_H/N_A)_0$. In the case of the rate-determining step of (3), a_N may remain lower than $a_{N,0}$ according to (9.b), even if its upper limit $a_{NH_3}/a_{H_2}^{3/2}$ exceeds $a_{N,0}$. By decreasing N_H/N_A in the latter case, however, a_N increases monotonously as seen from (5) written in

*) We have from the equilibria of (10) and (11), $a_{Fe}^4 a_{NH_3,0} = a_{Fe_4N} a_{H_2,0}^3$ and $a_{Fe}^4 a_{N,0} = a_{Fe_4N}$ in accordance with (6), and hence (12), where a_{Fe} and a_{Fe_4N} are absolute activities of the respective solid phases.

the form according to (8), as

$$a_{\text{NH}_3}/a_{\text{H}_2} = a_{\text{N}}a_{\text{H}_2}^{1/2} + k_2/k_1 \cdot a_{\text{N}}^2, \quad (13)$$

even to exceed $a_{\text{N},0}$. The a_{N} at the entrance increases thus monotonously with decrease of $N_{\text{H}}/N_{\text{A}}$ and attains $a_{\text{N},0}$ or remains below it, when $N_{\text{H}}/N_{\text{A}}$ just equals $(N_{\text{H}}/N_{\text{A}})_0$ according as (4) or (3) determines the rate. (α)

We consider next the variation of a_{N} along the flow through the catalyst's bed at the given $N_{\text{H}}/N_{\text{A}}$ for a definite state of catalyst's surface throughout. The left of (13) decreases monotonously along the flow, since a_{NH_3} decreases but a_{H_2} increases, as NH_3 decomposes to yield H_2 . The k_2/k_1 being definite for the definite state of the catalyst's surface, (13) states that a_{N} decreases steadily along the flow in the catalyst's bed. (β)

It follows from (α) and (β) that the catalyst's surface is secured definitely at the state of α -phase over the region, where $N_{\text{H}}/N_{\text{A}} > (N_{\text{H}}/N_{\text{A}})_0$ at the entrance of the catalyst's bed as well as at its interior.

Starting from the latter state, the $N_{\text{H}}/N_{\text{A}}$ may be decreased to some extent below $(N_{\text{H}}/N_{\text{A}})_0$ without causing a_{N} to exceed $a_{\text{N},0}$, keeping the previous state stable throughout according to (α), until $a_{\text{N},0}$ is surpassed by a_{N} first at the entrance to turn catalyst's surface there from α - into γ' -phase. Even then the catalyst's surface in the interior of the bed may remain stably at the state of α -phase according to (β). It follows besides from (IV), that the catalyst's surface at the entrance, if once turned into γ' -phase, carries forward the gas mixture of greater $a_{\text{NH}_3}/a_{\text{H}_2}^{3/2}$ to farther portion of the catalyst along the flow to promote nitridation there. The catalyst is thus nitrided progressively from the entrance toward the exit along with the decrease of $N_{\text{H}}/N_{\text{A}}$, resulting in the decrease of R by (IV) below its value which would be maintained, if the catalyst's surface remained at the state of α -phase whole throughout.

Let a) or b) be the curve of R versus $N_{\text{H}}/N_{\text{A}}$, which would be realized when the catalyst's surface were at the state of α - or γ' -phase respectively throughout. R descends thus from the curve a) with decrease of $N_{\text{H}}/N_{\text{A}}$, to the curve b), which lies below a) according to (IV). Let C be the point where R just meets the curve b). Increasing now $N_{\text{H}}/N_{\text{A}}$ from the value lower than that at C, R does not trace its former course beyond C, because a_{N} on γ' -phase is kept according to (9.a) equal to $a_{\text{NH}_3}/a_{\text{H}_2}^{3/2}$, which is higher than at $(N_{\text{H}}/N_{\text{A}})_0$ and hence sufficient to secure its present state of γ' -phase stable. But since $a_{\text{NH}_3}/a_{\text{H}_2}^{3/2}$ at the entrance decreases with increase of $N_{\text{H}}/N_{\text{A}}$ by (α) and $a_{\text{NH}_3}/a_{\text{H}_2}^{3/2}$ in the

interior of the catalyst's bed decreases along the flow by (β), a point must be arrived at with increase of N_H/N_A , where $a_N = a_{NH_3}/a_{H_2}^{3/2}$ decreases below $a_{N,0}$, first at the exit to reduce nitride there to α -phase and, with further increase of N_H/N_A , the reduction propagates toward the entrance. The R deviates now from the curve b) more and more upwards with the progress of the reduction according to (IV), until it returns to the curve a) at a point A, where the reduction is just completed at the entrance, i. e. at the composition $(N_H/N_A)_0$ of inflow gas, corresponding to the equilibrium of (10).

We now consider ϵ -phase in addition to α - and γ' -phase. Since a_N is kept constantly at $a_{NH_3}/a_{H_2}^{3/2}$ on γ' - as well as on ϵ -phase according to (II) and (9. a), the catalyst's surface is at the equilibrium, by (9. a) relevant to the composition of the gas mixture irrespective of the history. The transition from the curve b) to that appropriate to ϵ -phase or reverse should in consequence occur at $(N_H/N_A)_0'$, possibly with some rise or drop of R but without any stable hysteresis. Let b') be the R curve of nitrides consisting of b) and the curve of ϵ -phase thus conjugated. The foregoing argument for the curves a) and b) holds similarly with regard to the curves a) and b'), leading likewise to the necessary appearance of the stable hysteresis.

The above inference thus accounts for the observation, leading, on the one hand, to the attribution of the curves a) and b') respectively to those A'AB and ECD in Fig. 1, and requiring on the other hand, that the point A must lie on the vertical chain line γ', α , where the inflow gas is just in the equilibrium of (10) at the entrance as mentioned above, and that the transition from the curve b') to a) must be accompanied, because of the reduction, by an excess outflow of total nitrogen over its inflow, in the form of ammonia or nitrogen or both. The first requirement is fulfilled as seen from Fig. 1, while the second one verified by the experimental fact stated in § 1, that outflow rate of ammonia has exceeded its inflow rate, since the overall synthesis of ammonia is excluded thermodynamically at the present experimental condition.

§ 5 Discussion

1. The observed hysteresis has been accounted for on the basis of the postulates from (I) to (V) in § 2, which leads to the conclusion (β), § 4 that a_N decreases along the flow through the catalyst's bed. This conflicts, however, with one of consequences of the previous paper¹⁾,

that N(a) is in equilibrium with gaseous nitrogen and hence its activity increases with increase of nitrogen along the flow. The conflict is reconciled by modifying the above postulates, which defines the mechanism. Revised postulates are that, in place of (I), both the reactions on α -phase and nitrides, follow the sequence (2) whose third step is replaced by the two ones



and

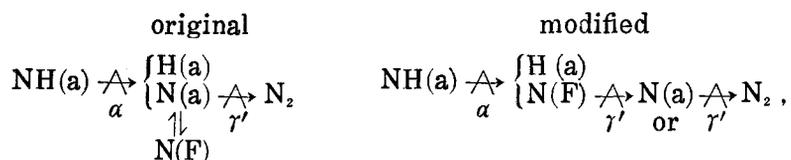


that, instead of (II), (14. a) is the rate-determining step on α -phase and either (14. b) or (4) is that on nitrides, that, rather than (III), the backward rate of (14. b) is negligible compared with its forward rate, and that, for (IV), the steady rate is smaller when governed by (14. b) or (4) than by (14. a), while (V) is eliminated. We have thus instead of (5)

$$V_s = k_1 (a_{\text{NH}} - a_{\text{N}} a_{\text{H}}) = k_2 a_{\text{N}},$$

where a_{N} denotes the absolute activity of N(F). The experimental results are quite similarly explained as in the foregoing section on the basis of the modified mechanism defined by the new postulates without conflicting with the above consequence of the previous paper¹⁾.

The original and the modified mechanisms are compared schematically with special reference to the replaced steps, as



where $\xrightarrow{\alpha}$ added to with α or γ' denotes the rate-determining step on α - or γ' -phase and \rightleftharpoons the equilibrium relation postulated by (V).

The modified mechanism will be investigated further in later works.

2. Present experimental results exclude, as shown below, the recombination $2\text{N(a)} \rightarrow \text{N}_2$ of adsorbed nitrogen atoms as the rate-determining step on α -phase, whether the step constitutes the original sequence (2) or the modified one, which step has hitherto been usually assumed to be rate-determining but recently negated by the determination of the stoichiometric number of the rate-determining step⁵⁾.

Let the recombination be the rate-determining step on α - as well as on γ' -phase. Eq. (9.a) holds then invariably irrespective of the state of the catalyst's surface for both the original and the modified sequence of steps mentioned above. The consequence is that the catalyst's surface turns quite reversibly from α - to γ' -phase or conversely according as a_N defined by (9.a) rises above or fall below $a_{N,0}$, leaving no possibility of hysteresis over the region of N_H/N_A where γ' -phase exists in equilibrium with gas, in contradiction to the observation. The conclusion is quite the same if the reaction be governed on γ' -phase by (14.b) instead, in the case of the modified sequence.

Next, we consider the case when the reaction is governed by the recombination (4) on α -phase but by any other step on γ' -phase, first on the basis of the original sequence. The absolute activity product of the initial complex of the rate-determining step must exceed that of the appropriate final complex, i. e. $a_{NH} > a_N a_H$ for the rate-determining step of (3), which has led to (9.b). We have, however, invariably (9.b), as readily be shown, by assuming any of the remaining three steps of the scheme (2) other than (3) and (4) as the rate-determining one and hence by rewriting any one of equal signs of (7) into that $>$ of inequality.

If then, the catalyst's surface begins to turn into γ' - from α -phase, as soon as a_N , which equals $a_{NH_3}/a_{H_2}^{3/2}$ on α -phase according to the premise, increases above $a_{N,0}$. But since γ' -phase causes to depress a_N below $a_{NH_3}/a_{H_2}^{3/2}$ so that α -phase is recovered but it turns again into γ' -phase and so on. The catalyst's surface thus oscillates between the states of α - and γ' -phase over a certain range of $a_{NH_3}/a_{H_2}^{3/2}$ or of N_H/N_A , where $a_{N,0}$ lies between $a_{NH_3}/a_{H_2}^{3/2}$ and the value of a_N kinetically reduced below $a_{NH_3}/a_{H_2}^{3/2}$ on γ' -phase. The oscillation may be only microscopic to reveal macroscopically a steady state apparently observed. But then the effect of the history of the catalyst's surface is extinguished, never giving rise to any stable hysteresis over the N_H/N_A -region, where γ' -phase is in equilibrium with gas, in conflict with the observation.

Just the same consequence is arrived at on the basis of the modified sequence assuming that the rate-determining step is the recombination (4) on α -phase but any step of the sequence other than (14.b) and (4) on γ' -phase. The final conclusion is that the recombination of nitrogen atoms can not be assumed as the rate-determining step on α -phase without opposing the observation, whether based on the original or the modified sequence.

Summary

Hydrogen-ammonia mixture of different definite compositions was allowed to flow through a catalyst's bed used in the previous experiment (Ref. 2) at 487°C and 1 atm total pressure, and the resulting percent R of ammonia decomposition at the steady state finally attained was observed similarly as in the previous experiment (*loc. cit.*), keeping the inflow rate N_A of ammonia at 70 cc NTP min⁻¹ and successively increasing or decreasing that N_H of hydrogen from one to the other observation. It was thus found that R reveals a stable hysteresis.

The hysteresis was satisfactorily accounted for on the basis of a slight modification of the mechanism concluded in the foregoing paper (Ref. 1) and of the known phase equilibrium of iron-nitrogen system (Refs. 6, 7 and 9), and shown to defy the rate-determining step of the recombination of adsorbed nitrogen atoms in accordance with the conclusion of the previous works (Refs. 5 and 1).

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