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(Note)

THE STOICHIOMETRIC NUMBER OF THE RATE-DETERMINING STEP OF AMMONIA DECOMPOSITION OVER NICKEL CATALYST

By

Akio KAZUSAKA*)

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The stoichiometric number of the rate-determining step, ν_r, of the ammonia decomposition or synthesis,

$$2NH_3 = N_2 + 3H_2, \qquad (1)$$

over a doubly-promoted iron catalyst has been determined as two by ENOMOTO and his coworkers.[1,2] On the basis of this result and the assumed sequence of steps,

$NH_3 \longrightarrow NH_2(a)+H(a)$	2	(2. I)
$NH_2(a) \longrightarrow NH(a)+H(a)$	2	(2. II)
$NH(a) \longrightarrow N(a)+H(a)$	2	(2. III)
$2H(a) \longrightarrow H_2$	3	(2. IV)
$2N(a) \longrightarrow N_2$	1	(2. V)

they have concluded that the rate-determining step is one of the dehydrogenation steps (2.I), (2.II) and (2.III) rather than the step of nitrogen desorption (2. V). In the above steps, the (a) denoted the adsorbed state of the species to which attached, and the number annexed to each step was the stoichiometric number of the appropriate step.

Later works made by BOKHOVEN, GORGELS and MARS,[3] TANAKA, YAMAMOTO and MATSUYAMA[4], TANAKA[5], and the present author and TANAKA[6], with respect to reaction (1) over a singly- or doubly-promoted iron catalyst have led the ν_r-value of unity, and their result suggests that the step (2.V) controlls the rate of reaction (1) in contrast with the former conclusion.

TANAKA[7], and the present author and TANAKA[6] have assured their conclusion by evaluation of the atomic fraction of heavy nitrogen in the adsorbed nitrogen made simultaneously with the determination of ν_r in course of the decomposition

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

of ^{15}N-enriched ammonia. In the present work, the same method of kinetic observation is applied to ammonia decomposition over a nickel catalyst.

Experimentals

The experimental apparatus used was similar to that employed previously[6].

The nickel catalyst was prepared from nickel oxide (5.82 and 5.81 gr. for runs in Series 2 and 3, and runs in Series 4, respectively), which was obtained by calcination of nickel carbonate in air at 500°C for 24 hours. The nickel oxide was then mixed with cracked chips of quartz*), reduced in the quartz reaction vessel by circulating hydrogen at a pressure of 60 to 70 cmHg at 500°C for 24 hours, and finally degassed to less than 1×10^{-5} mmHg at room temperature.

The absence of the catalytic activity of the reaction apparatus without catalyst was ascertained by preliminary runs of Series 1 as shown in the Table.

Runs in Series 2 and 4 were conducted to determine the ν_r-value and the atomic fraction of heavy nitrogen in the adsorbed nitrogen in course of decomposition at 470 and 440°C respectively. The reaction gas for these Series contained initially ^{15}N-enriched ammonia of *ca.* 15 mmHg, and a 3 : 1 mixture of H_2 and N_2 of 1285 mmHg. Runs in Series 3 were a synthesis of ammonia at 470°C from a 3 : 1 mixture of H_2 and N_2 of 1300 mmHg. From the results of runs in Series 2 and 3, we could estimated the equilibrium constant of reaction (1) at 470°C. The change in partial pressure of ammonia and the isotopic exchange of nitrogen were followed as detailed previously.[6]

Results and discussion

The results obtained are summarized in the Table 1, from which the ν_r and the atomic fraction of heavy nitrogen in the adsorbed nitrogen were evaluated as follows.

The stoichiometric number of the rate-determining step of ammonia decomposition (1) is given[5,6] as

$$\nu_r = \frac{\log (P_A^2/P_H^3 P_N \cdot K)}{\log\{1+(Z^A-Z^N)\,\mathrm{d}\ln P_A/dZ^A\}}, \qquad (3)$$

where P_A, P_H or P_N is the partial pressure of ammonia, hydrogen or nitrogen, Z^A or Z^N the atomic fraction of heavy nitrogen in gaseous ammonia or nitrogen, and K the equilibrium constant of the decomposition (1), respectively. Because the initial values of P_H and P_N were much larger than P_A in the present work as described in the section of Experimentals, we can consider P_H and P_N to be constant in course of decomposition as compared with P_A. So Eq. (3) can be

*) The mixing with quartz chips was necessary for the reaction gas to flow easily through the catalyst bed.

TABLE 1. Kinetic Data for Ammonia Synthesis and Decomposition, as well as Nitrogen Exchange
(Symbols of P_A etc. are interpreted in the text.)

No. of run	t*) (hours)	P_A (mmHg)	Z_A (%)	$Z^{N(a)}$ (%)	Z^N (%)	Z_1^N (%)	Z_2^N (%)	ν_r
Series 1. Blank runs without catalyst, 470°C.								
0	0	15.26	—		0.004	0.008	0	
1	0.50	15.24	0.920		0.004	0.008	0	
2	1.54	15.29	0.922		0.004	0.008	0	
3	3.16	15.25	0.918		0.004	0.008	0	
4	5.42	15.14	0.924		0.004	0.007	0	
5	7.76	15.02	0.920		0.004	0.008	0	
Series 2. Determination of ν_r in a decomposition at 470°C according to Eq. (5)								
0	0	15.21	0.910	0.95	0.008	0.010	0.004	—
1	1.20	10.80	0.890	0.92	0.014	0.011	0.008	1.1
2	4.50	5.11	0.821	0.80	0.023	0.013	0.016	1.0
3	7.94	3.42	0.757	0.69	0.025	0.013	0.018	0.9
4	11.55	2.32	0.600	0.55	0.027	0.015	0.019	0.8
5	20.85	1.99	0.374	—	0.030	0.018	0.021	—
6	30.85	2.01	0.245	—	0.030	0.019	0.021	—
Series 3. Synthesis, 470°C.								
0	0	0.00						
1	0.62	0.27						
2	1.26	0.51						
3	2.58	0.99						
4	5.30	1.49						
5	9.54	1.87						
6	17.09	2.02						
Series 4. Determination of ν_r in a decomposition at 440°C according to Eq. (4)								
0	0	15.92	0.891	0.94	0.004	0.009	0	
1	0.64	15.75	0.921	0.94	0.004	0.008	0	
2	3.32	15.39	0.918	0.93	0.006	0.009	0.002	
3	10.82	14.69	0.917	0.91	0.007	0.009	0.003	
4	25.64	13.20	0.912	0.88	0.008	0.008	0.004	1.0
5	56.13	11.04	0.895	0.86	0.012	0.009	0.008	
6	87.73	9.86	0.887	0.84	0.016	0.011	0.011	
7	121.13	8.38	0.870	0.82	0.016	0.011	0.011	
8	156.53	7.55	0.845		0.018	0.011	0.012	

*) Reaction time corrected with respect to the pressure decrease of the reaction system. See ref. 6 or 11.

approximated as

$$\log\left\{1+(Z^{A}-Z^{N})\,\mathrm{d}\ln P^{A}/dZ^{A}\right\}=\frac{2}{\nu_r}\log P_A+\text{constant}, \tag{4}$$

or in its integral form as

$$\int_{Z^A}^{(Z^A)_0}\frac{dZ^A}{Z^A-Z^N}=\frac{2.30}{2}\nu_r\log\left[\frac{(P_A)_0^{2/\nu_r}}{\left\{\frac{(P_A)_0^2K}{(P_H)_0^3(P_N)_0}\right\}^{1/\nu_r}-1}\,\frac{\left\{\frac{P_2^AK}{(P_H)_0^3(P_N)_0}\right\}^{1/\nu_r}-1}{(P_A)^{2/\nu_r}}\right] \tag{5}$$

The $(Z^A)_0$ *etc.* in Eq. (5) are the initial value of Z^A *etc.*. The ν_r-value can be estimated according to Eq. (4) from the slope of the logarithmic plot of $\{1+(Z^A-Z^N)\,\mathrm{d}\ln P_A/dZ^A\}$ against P_A, in which $\mathrm{d}\ln P_A/dZ^A$ is given as the slope of the curve of $\ln P_A$ *vs.* Z^A. Eq. (4) is thus convenient for the estimation of ν_r in a case where the equilibrium constant, K, is unknown. In Eq. (5), on the other hand, the term of the left-hand side can be estimated graphically, and we can obtain the most fitting value of ν_r satisfied by Eq. (5) by trial and error. Containing no differential term of $\mathrm{d}\ln P_A/dZ^A$, this integral form gives us more correct value of ν_r than Eq. (4).

With respect to the homomolecular isotopic exchange of nitrogen by step (2. V), we have

$$d(P_NZ_1^N)/dt=\left\{2Z^{N(a)}(1-Z^{N(a)})\right\}v_+-Z_1^Nv_- \tag{6. I}$$

and

$$d(P_NZ_2^N)/dt=(Z^{N(a)})^2v_+-Z_2^Nv_-, \tag{6. II}$$

where Z_1^N or Z_2^N is the mole fraction of $^{29}N_2$ or $^{30}N_2$, $Z^{N(a)}$ the atomic fraction of heavy nitrogen in the adsorbed nitrogen, v_+ or v_- the forward or backward rate of step (2. V), respectively. In the steady state of reaction (1), where $dP_N/dt=v_+-v_-$, the $Z^{N(a)}$ is given from Eqs. (6) as

$$Z^{N(a)}=\frac{\left(\frac{dZ_2^N}{dZ_1^N}\right)+\sqrt{\left(\frac{dZ_2^N}{dZ_1^N}\right)^2-\left(1+2\frac{dZ_2^N}{dZ_1^N}\right)\left(Z_1^N\frac{dZ_2^N}{dZ_1^N}-Z_2^N\right)}}{1+2\frac{dZ_2^N}{dZ_1^N}} \tag{7}$$

The equilibrium pressure of ammonia is *ca.* 2 mmHg as obtained by the results of Series 2 and 3 given in the Table 1, and hence the equibrium constant, K, is evaluated at *ca.* 7.24×10^{10} mmHg^2 at 470°C. The ν_r-values are calculated according to Eq. (5) with respect to this K-value and the experimental results of Series 2 as given in the last column of the Table 1. They are all close to unity. Logarithmic plots of $\{1+(Z^A-Z^N)\mathrm{d}\ln P_A/dZ^A\}$ against P_A for Series 4 at 440°C

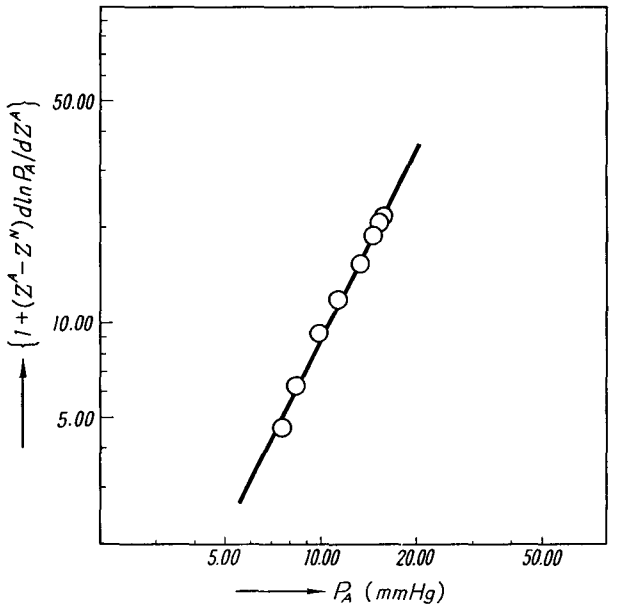

Fig. 1. Logarithmic plots of $\{1+(Z^A-Z^N)d\ln P_A/dZ^A\}$ against P_A for Series 4.

are shown in Fig. 1, from which the ν_r-value is estimated as unity according to Eq. (4).

The $Z^{N(a)}$ in runs both of Series 2 (470°C) and 4 (440°C) are evaluated according to Eq. (7) to be close to Z^A but not Z^N as listed on the 5th column of the Table 1. These results show that the adsorbed nitrogen are practically equilibriated with gaseous ammonia. It is thus concluded that the desorption of the adsorbed nitrogen (2. V) is the rate-determining step of the decomposition on the nickel catalyst. This conclusion is in agreement with those by KEMBALL *et al.*,[8] TAMARU *et al.*,[9] and TAKEZAWA.[10]

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