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**PROMOTER ACTION OF POTASSIUM OXIDE IN
AMMONIA SYNTHETIC IRON CATALYST**

By

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It has been proposed that the rate of ammonia decomposition over ammonia synthetic iron catalysts is controlled by the desorption of adsorbed nitrogen¹⁾. The observation of the stoichiometric number, however, suggested the dehydrogenation step of $\text{NH}_3(\text{a})$, $\text{NH}_2(\text{a})$ or $\text{NH}(\text{a})$ to be rate-determining, where (a) denotes the adsorbed state²⁾.

As to this disagreement, we showed on the basis of kinetics of this reaction that the reaction mechanism may depend upon the reaction temperature³⁾ and also the content of potassium oxide promoter in ammonia synthetic iron catalyst⁴⁾.

In this work the promoter action of potassium oxide in ammonia synthetic iron catalyst was studied by applying the method of stoichiometric number of the rate-determining step ν_r to the ammonia decomposition.

The experimental apparatus and procedures were similar to those used in the previous works^{5,6)}. Four kinds of iron catalyst were prepared in the usual method at Government Chemical Industrial Research Institute, Tokyo, and the content of potassium oxide in them was varied from 0 to 1.54 wt % with the fixed amount of alumina as shown in Table 1. Catalyst used was amounted

TABLE 1. Composition of Catalyst before Reduction. (wt %)

Catalyst No.	Substance			
	Total Iron	Al_2O_3	K_2O	SiO_2
1	70.47	2.69	—	0.09
2	69.95	2.55	0.33	0.09
3	69.41	2.53	0.58	0.15
4	67.42	2.39	1.54	0.13

between 0.4 and 1.5 gr. depending on their activity and was from 12 to 20 mesh size.

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The catalysts were reduced preliminarily at 600°C for 72 hr in a purified hydrogen at a flow rate of 500 cc/min. Decomposition reaction of ¹⁵N-enriched ammonia was carried out at 361°C. The reaction gas was a 3:1 mixture of hydrogen and nitrogen besides *ca.* 15 mmHg ¹⁵N-enriched ammonia. The total pressure was kept at 750 mmHg during the reaction. Nitrogen and hydrogen were purified by the same method as described previously^{3,4}.

Table 2 shows the observed results. In the present experimental conditions, three kinds of reaction proceeded concurrently; the ammonia decomposition, the

TABLE 2. Kinetic Data for Ammonia Decomposition, at 361°C

Catalyst No.	<i>t</i> [*] (hours)	<i>P</i> _A (mmHg)	<i>Z</i> ^A (%)	<i>Z</i> ^{N(a)} (%)	<i>Z</i> ^N (%)	<i>Z</i> ₁ ^N (%)	<i>Z</i> ₂ ^N (%)
1 (1.49 gr)	0	13.58	83.4	82.6	1.71	1.40	1.00
	0.97	10.46	79.2	78.8	2.61	1.72	1.75
	2.29	7.42	—	68.9	3.44	2.15	2.37
	5.62	5.32	35.2	27.3	4.68	3.39	2.99
	8.91	5.09	21.1	10.5	5.00	8.10	2.97
2 (0.42 gr)	0	14.26	—	87.5	1.43	1.60	0.634
	3.46	13.65	83.1	86.6	1.72	1.65	0.886
	14.33	11.20	79.2	79.5	2.47	1.94	1.50
	35.22	8.09	63.0	64.5	3.55	2.51	2.30
	50.17	7.03	60.9	53.3	4.03	2.91	2.58
3 (0.52 gr)	0	16.23	93.4	96.7	0.478	0.755	0.0996
	0.69	14.60	94.5	95.2	1.06	0.810	0.601
	2.24	12.36	92.6	92.6	1.69	0.877	1.25
	5.51	8.96	85.2	87.5	2.72	1.06	2.19
	8.52	6.90	76.3	80.5	3.35	1.28	2.71
4 (1.29 gr)	0	20.18	96.9	—	0.348	0.697	0
	0.72	19.84	97.4	97.5	0.456	0.568	0.172
	3.74	16.94	95.3	96.5	1.72	0.610	1.00
	9.68	12.53	90.9	93.5	2.55	0.722	2.20
	14.81	9.41	83.3	—	3.55	1.01	3.04

*) The reaction time is corrected for the change of volume of the reaction system during the time course of the reaction. See ref. (5).

exchange reaction of ¹⁵N between ammonia and nitrogen gas, and the nitrogen isotope equilibration reaction.

The forward and backward unidirectional rates, *V*₊ and *V*₋, of ammonia

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decomposition were evaluated from the results of the ammonia decomposition and the accompanying nitrogen exchange of ^{15}N between ammonia and nitrogen gas as follows. The net rate of decomposition is given as

$$-\frac{dP_A}{dt} = V_+ - V_-, \quad (1)$$

where P_A the partial pressure of ammonia and t the reaction time. The rate of decrease of ^{15}N -enriched ammonia is given as

$$-\frac{1}{2} \frac{d(P_A Z^A)}{dt} = Z^A V_+ - Z^N V_-, \quad (2)$$

where Z^A or Z^N is the respective atomic fraction of ^{15}N in ammonia or nitrogen gas. Solving the above equations and $Z^A P_A + 2Z^N P_N = \text{const.}$ with respect to V_+ and V_- , we have

$$V_+ = \frac{P_N}{Z^A - Z^N} \frac{dZ^N}{dt} \quad (3.1)$$

and

$$V_- = -\frac{1}{2} \frac{P_A}{Z^A - Z^N} \frac{dZ^A}{dt}, \quad (3.2)$$

where P_N is the partial pressure of nitrogen. Figure 1 shows the logarithmic plots of V_+ and V_- against P_A^* . They are found to be nearly proportional to P_A and $1/P_A$, respectively, for every catalyst except the No. 4 catalyst.

The ν_r -value is defined as⁷⁾

$$\nu_r = \frac{-\Delta F}{RT \ln V_+/V_-}, \quad (4)$$

where $-\Delta F$ is the chemical affinity of the reaction and R or T has the usual meaning. The partial pressures of nitrogen and hydrogen were almost kept constant during the time course of the reaction, hence Eq. (4) is approximated as⁶⁾

$$\log V_+/V_- = 2/\nu_r \log P_A + \text{const.} \quad (4')$$

Figure 2 shows this relation, from which the ν_r -value were estimated at nearly unity for every catalyst. This result is in agreement with those observed by TANAKA *et al.*⁸⁾ or one of the present authors and TANAKA⁵⁾ over the singly- or doubly-promoted iron catalysts, respectively.

*) It is difficult to obtain graphically the value of the factor, $\frac{dZ^N}{dt}$, in Eq. (3.1). Therefore V_+ was evaluated by substituting V_- into Eq. (1) instead of using Eq. (3.1). The V_- was evaluated by Eq. (3.2).

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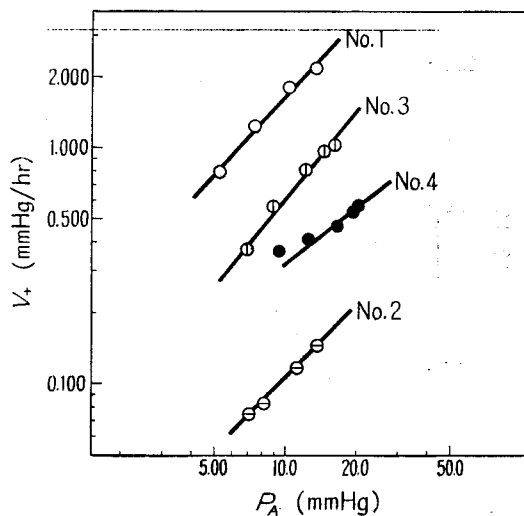


Fig. 1 a. The relation between V_+ and P_A .

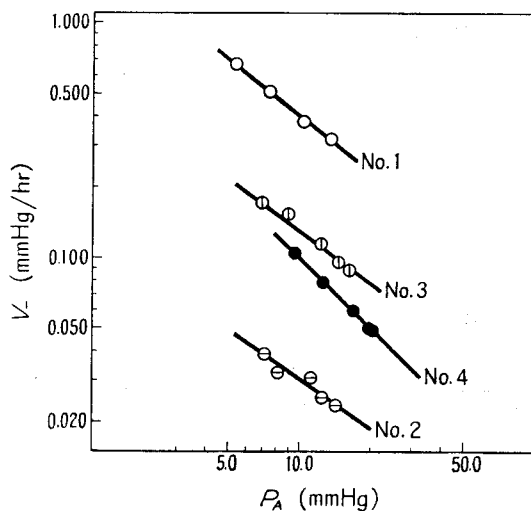


Fig. 1 b. The relation between V_- and P_A .

In connection with the mechanism of ammonia decomposition, it is interesting to compare the rate of nitrogen isotope equilibration reaction, $^{28}\text{N}_2 + ^{30}\text{N}_2 = 2^{29}\text{N}_2$, with that of ammonia decomposition. The formation rate of $^{29}\text{N}_2$ or $^{30}\text{N}_2$ is given as

$$\frac{d(P_N Z_i^N)}{dt} = 2Z^{N(a)}(1 - Z^{N(a)})v_+ - Z_i^N v_- \quad (5.1)$$

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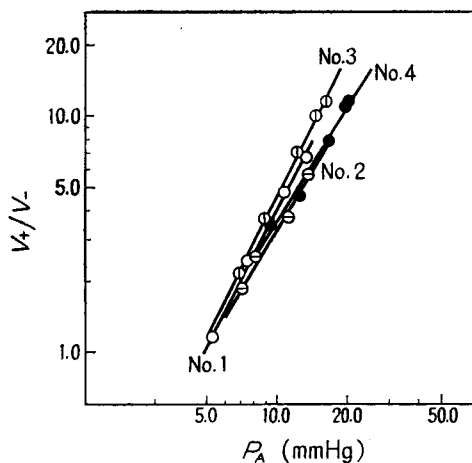


Fig. 2. The relation between V_+/V_- and P_A .

or

$$\frac{d(P_N Z_2^N)}{dt} = \{Z^{N(a)}\}^2 v_+ - Z_2^N v_-, \quad (5.2)$$

where v_+ or v_- is the desorption or adsorption rate of nitrogen, Z_1^N or Z_2^N the mole fraction of $^{29}\text{N}_2$ or $^{30}\text{N}_2$ in nitrogen gas and $Z^{N(a)}$ the atomic fraction of ^{15}N in the adsorbed nitrogen, respectively. Solving Eq. (5), $\frac{dP_N}{dt} = v_+ - v_-$ and $Z^A P_A + 2Z^N P_N = \text{const.}$ with respect to v_+ , v_- and $Z^{N(a)}$, where $Z^N = 1/2 Z_1^N + Z_2^N$, we have

$$v_+ = \frac{P_N}{Z^{N(a)} - Z^N} \frac{dZ^N}{dt}, \quad (6.1)$$

$$v_- = \frac{1}{Z^{N(a)} - Z^N} \left[-\frac{1}{2} P_A \frac{dZ^A}{dt} - \frac{1}{2} (Z^A - Z^{N(a)}) \frac{dP_A}{dt} \right] \quad (6.2)$$

and

$$Z^{N(a)} = \frac{\left(\frac{dZ_2^N}{dZ_1^N}\right) \pm \sqrt{\left(\frac{dZ_2^N}{dZ_1^N}\right)^2 - \left\{1 + 2\left(\frac{dZ_2^N}{dZ_1^N}\right)\right\} \left\{Z_1^N \left(\frac{dZ_2^N}{dZ_1^N}\right) - Z_2^N\right\}}}{1 + 2\left(\frac{dZ_2^N}{dZ_1^N}\right)}. \quad (6.3)$$

From Eq. (3) and (6), we have

$$\frac{v_+}{V_+} = \frac{Z^A - Z^N}{Z^{N(a)} - Z^N} \quad (7.1)$$

and

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$$\frac{v_-}{V_-} = \frac{Z^A - Z^N}{Z^{N(a)} - Z^N} \left\{ 1 - \frac{Z^A - Z^{N(a)}}{Z^{N(a)} - Z^N} \frac{dP_A}{dZ^A} \right\}. \quad (7.2)$$

The evaluated values of $Z^{(a)}$ is found to be nearly equal to Z^A as shown in Table 2. The ratios of v_+/V_+ and v_-/V_- are thus close to unity, that is, each unidirectional rate of ammonia decomposition is equal to that of nitrogen equilibration reaction for every catalyst. This result gives the conclusion that both the reactions are rate-determined by the same step.

In the previous paper⁴⁾ we found that the rate expression of ammonia decomposition changed from $k(P_A/P_H^{0.5})^\alpha$ to $k'(P_A/P_H^{1.5})^\beta$ by the increase of the amount of potassium oxide promoter, where k , k' , α and β are the constants and P_H is the partial pressure of hydrogen. These results were explained to be caused by the change of the rate-determining step from the step (8.2) to the step (8.5) of the following reaction scheme:



The number annexed to each steps is the stoichiometric number. According to the above explanation the ν_r -value must change from two to unity by increasing the content of K_2O . This is not agreeable to the observed results of the ν_r -value in the present investigation.

We further found that the rate of nitrogen isotope equilibration reaction was affected by the presence of hydrogen over the No. 1 catalyst but not over the No. 2, No. 3 and No. 4 catalysts⁹⁾. On the basis of these findings it was concluded that the surface of the No. 1 catalyst might be covered by hydrogenated nitrogen, whereas the surface of the No. 2, No. 3 or No. 4 catalyst might be covered by adsorbed nitrogen, that is, the mechanism proposed by TEMKIN and PYZHEV¹⁾ was valid in the case of the No. 2, No. 3 and or No. 4 catalyst, but not over No. 1 catalyst.

Consequently, the scheme (8) with the rate-determining step (8.5) is agreeable to the result obtained over the No. 2, No. 3 or No. 4 catalyst, but not that obtained over the No. 1 in the present experimental conditions.

The amount of potassium oxide promoter thus affects severely the reaction mechanism of ammonia decomposition, changing the adsorbed species on the catalyst surface. This conclusion is in conformity with that of the previous kinetic study⁴⁾.

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