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THE MECHANISM OF CATALYZED DECOMPOSITION OF AMMONIA IN THE PRESENCE OF COMMERCIAL DOUBLY PROMOTED IRON CATALYST

By

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Abstract

Kinetic observations on ammonia decomposition by the present authors are analyzed in terms of generalized theory of reaction rate under the assumption that the decomposition proceeds through the sequence of steps, $\text{NH}_3 \rightarrow \text{NH}_2(\text{a}) + \text{H}(\text{a})$, $\text{NH}_2(\text{a}) \rightarrow \text{NH}(\text{a}) + \text{H}(\text{a})$, $\text{NH}(\text{a}) \rightarrow \text{N}(\text{a}) + \text{H}(\text{a})$, $2\text{N}(\text{a}) \rightarrow \text{N}_2$, and $2\text{H}(\text{a}) \rightarrow \text{H}_2$, where (a) signifies the adsorbed state.

The rate of decomposition is formulated allowing for repulsive interactions among adsorbates inclusive of the critical complex of rate-determining step by the proportional approximation. From the observed pressure dependences of the rate upon ammonia, hydrogen and nitrogen, it is concluded that the rate-determining step of the decomposition around 425°C is the desorption of nitrogen adatoms $2\text{N}(\text{a}) \rightarrow \text{N}_2$, which is consistent with the observation of stoichiometric number of rate-determining step. This conclusion is further confirmed, by the agreement of the activation heat of decomposition deduced according to the conclusion with observation and by the agreement of the number of sites of the critical complex similarly derived with the crystallographic value. The pressure dependences of the rate around 480°C, on the other hand, lead to the conclusion that the rate-determining step is the dehydrogenation of the adsorbed amino group, $\text{NH}_2(\text{a}) \rightarrow \text{NH}(\text{a}) + \text{H}(\text{a})$.

The rate-determining step thus shifts with rise of temperature from the desorption of nitrogen adatoms to the dehydrogenation of adsorbed amino group.

Introduction

The mechanism of ammonia decomposition over commercial iron catalyst is frequently discussed on the basis of the Temkin-Pyzhev equation, as derived from the assumption of nitrogen desorption determining the rate.¹⁻⁴⁾

Some doubt has recently been cast upon this mechanism by findings on the stoichiometric number of rate-determining step,⁵⁾ on analysis of the expe-

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rimental results of ammonia decomposition,⁶⁻⁷⁾ inclusive of the hysteresis⁸⁾ due to the change of catalyst's surface,⁹⁾ and on the adsorption of nitrogen and hydrogen in the course of synthesis or decomposition of ammonia.¹⁰⁾ These observations suggest that there may be operative, depending on the condition, some other mechanism than that prevailingly accepted.

Present authors conducted kinetic observation of ammonia decomposition anew¹¹⁻¹⁴⁾ with a view to elucidating matters, and established the different dependences of decomposition rate upon the partial pressures at different temperatures, namely

$$V_+ = k_1 \left\{ \frac{P_{\text{NH}_3}}{(P_{\text{H}_2})^{1.5}} \right\}^\alpha \quad \text{at about } 425^\circ\text{C}$$

and

$$V_+ = k_2 \left\{ \frac{P_{\text{NH}_3}}{(P_{\text{H}_2})^{0.5}} \right\}^\beta \quad \text{at about } 480^\circ\text{C}$$

where k_1 , k_2 , α , and β are constants, and P_{N_2} and P_{H_2} partial pressures of ammonia and hydrogen, respectively.

The present work is concerned with a statistical-mechanical analysis of these observations allowing for the repulsive interactions among adsorbates inclusive of the critical complex of rate-determining step.

1. The Rate of Heterogeneous Step (Heterogeneous Elementary Reaction)

The forward and backward rates, v_{+s} and v_{-s} , of a heterogeneous step, s , are statistical-mechanically expressed¹⁵⁾ as

$$v_{+s} = \kappa \left(\frac{kT}{h} \right) N_1^* q^* \theta_{\sigma^*} a^I, \quad (1.1. v_+)$$

and

$$v_{-s} = \kappa \left(\frac{kT}{h} \right) N_1^* q^* \theta_{\sigma^*} a^F, \quad (1.1. v_-)$$

where κ is the transmission coefficient, T the absolute temperature, h or k Planck's or Boltzmann's constant respectively, N_1^* , the number of sites, σ^* , per cm^2 for the critical complex, θ_{σ^*} , the probability that the site, σ^* , is vacated, and q^* the Boltzmann factor of reversible work w^* required to form the critical complex from its constituents in their respective standard states on a preliminarily vacated, definite σ^* , *i. e.*

$$q^* = \exp(-w^*/RT). \quad (1.2)$$

The a^I and a^F represent the absolute activities of the initial system, I, and the final system, F, of s , respectively and are reciprocal Boltzmann factors

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of the respective chemical potentials, μ^I and μ^F , of I and F, *i.e.*

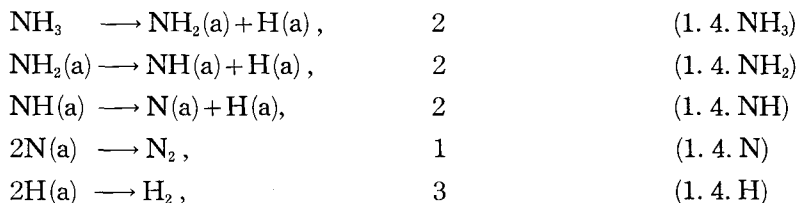
$$a^I = \exp(\mu^I/RT) \quad (1.3. a^I)$$

and

$$a^F = \exp(\mu^F/RT). \quad (1.3. a^F)$$

Eqs. (1.1) are developed below allowing for repulsive interactions among adsorbates inclusive of critical complex¹⁶⁻²⁰⁾ under the following assumptions.

(I) The decomposition proceeds through a sequence of steps,



one of them being the rate-determining step, where the stoichiometric numbers are attached to respective steps, and (a) signifies adsorbed state.

(II) The repulsive potential of an adsorbate, inclusive of the critical complex of heterogeneous step, is practically due to adsorbates of a single kind, $\delta(\text{a})$, exclusive of the critical complex; the single kind depends on the experimental condition.

(III) The repulsive potential of the adsorbate mentioned in (II), is proportional to the coverage of δ , $\theta_{\sigma(\delta)}$, which equals the probability that δ occupies its site of adsorption, σ .

(IV) The σ is practically either unoccupied or occupied by $\delta(\text{a})$ exclusively, hence

$$\theta_{\sigma(\delta)} + \theta_{\sigma(\delta)} = 1,$$

where $\theta_{\sigma(\delta)}$ is the probability of σ being unoccupied; the occupation of σ by the critical complex is negligible.

(V) The site of critical complex, σ^* , of a step consists of n adjacent sites, σ , of $\delta(\text{a})$.

The reversible work, w^* , is expressed in accordance with (II) and (III) as

$$w^* = w_0^* + u^* \theta_{\sigma(\delta)},$$

where w_0^* is the particular value of w^* at $\theta_{\sigma(\delta)}=0$ and u^* is the free energy increase due to repulsion between the critical complex and surrounding $\delta(\text{a})$ at $\theta_{\sigma(\delta)}=1$; w_0^* is given in terms of energy ϵ_0^* and entropy s_0^* of the critical complex at $\theta_{\sigma(\delta)}=0$ as $w_0^* = \epsilon_0^* - T s_0^*$, hence

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$$w^* = \varepsilon_0^* - Ts_0^* + u^* \theta_{\sigma(\delta)}. \quad (1.5)$$

Eqs. (1.1. v_+), (1.2) and (1.5) lead to the expression

$$v_{+,s} = \kappa \left(\frac{kT}{h} \right) N_1^* \theta_{\sigma(0)}^* a^I e^{s_0^*/R} e^{-\frac{\varepsilon_0^* + u^* \theta_{\sigma(\delta)}}{RT}}. \quad (1.6)$$

We have on the other hand¹⁵⁾

$$\theta_{\sigma(\delta)} / \theta_{\sigma(0)} = q^{\delta(a)} a^{\delta(a)}, \quad (1.7)$$

where $a^{\delta(a)}$ is the absolute activity of $\delta(a)$ given in terms of its chemical potential, $\mu^{\delta(a)}$, as

$$a^{\delta(a)} = \exp(\mu^{\delta(a)} / RT), \quad (1.8)$$

and $q^{\delta(a)}$ is the Boltzmann factor of the reversible work, $w^{\delta(a)}$, required to form $\delta(a)$ from its constituents in their respective standard states on its preliminarily vacated definite site, σ , *i. e.*

$$q^{\delta(a)} = \exp(-w^{\delta(a)} / RT). \quad (1.9)$$

The reversible work, $w^{\delta(a)}$, is expressed according to (II) and (III), similarly to (1.5), as

$$w^{\delta(a)} = \varepsilon_0^{\delta(a)} - Ts_0^{\delta(a)} + u\theta_{\sigma(\delta)}, \quad (1.10)$$

where $\varepsilon_0^{\delta(a)}$ and $s_0^{\delta(a)}$ represent the energy and the entropy of $\delta(a)$ at $\theta_{\sigma(\delta)}=0$, and u is the free energy increase due to the repulsion between $\delta(a)$ and surrounding adsorbates of the same kind at $\theta_{\sigma(\delta)}=1$. It follows from (1.7), (1.9) and (1.10) that

$$\theta_{\sigma(\delta)} / \theta_{\sigma(0)} = a^{\delta(a)} e^{s_0^{\delta(a)}/R} e^{-\frac{\varepsilon_0^{\delta(a)} + u\theta_{\sigma(\delta)}}{RT}}, \quad (1.11)$$

hence according to (IV)

$$\theta_{\sigma(\delta)} / (1 - \theta_{\sigma(\delta)}) = a^{\delta(a)} e^{s_0^{\delta(a)}/R} e^{-\frac{\varepsilon_0^{\delta(a)} + u\theta_{\sigma(\delta)}}{RT}}, \quad (1.12)$$

or

$$\theta_{\sigma(\delta)} = \frac{RT}{u} \ln \left\{ \frac{1 - \theta_{\sigma(\delta)}}{\theta_{\sigma(\delta)}} a^{\delta(a)} \exp \left(-\frac{\varepsilon_0^{\delta(a)} - Ts_0^{\delta(a)}}{RT} \right) \right\}. \quad (1.13)$$

Substituting $\theta_{\sigma(\delta)}$ from (1.13) into (1.6) and replacing $\theta_{\sigma(0)}^*$ approximately with $(1 - \theta_{\sigma(\delta)})^{n,*}$ we have

$$v_{+,s} = \kappa \left(\frac{kT}{h} \right) N_1^* (1 - \theta_{\sigma(\delta)})^{n-r} \theta_{\sigma(\delta)}^r e^{\frac{s_0^* - r s_0^{\delta(a)}}{R}} \cdot \frac{a^I}{(a^{\delta(a)})^r} e^{-\frac{\varepsilon_0^* - r \varepsilon_0^{\delta(a)}}{RT}}, \quad (1.14)$$

*) This replacement is exact in the absence of interaction among $\delta(a)$.

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where

$$\gamma = u^* / u. \quad (1.15)$$

The entropy $s_0^{\delta(a)}$ is expressed²¹⁾ statistical-mechanically in the cases of immobile and mobile adsorption of $\delta(a)$ assuming high enough vibrational frequencies, in the former case, as

$$s_0^{\delta(a)} = 0, \quad (\text{immobile adsorption}) \quad (1.16.i)$$

and

$$s_0^{\delta(a)} = R \ln A^{\delta(a)} (2\pi m^{\delta(a)} kT/h). \quad (\text{mobile adsorption}) \quad (1.16.m)$$

The argument of the logarithmic function on the right-hand side of (1.16.m) represents the partition function of the two-dimensional translation parallel to the catalytic surface over an area, $A^{\delta(a), *}$ and $m^{\delta(a)}$ is the mass of $\delta(a)$.

2. The Rate Equation

The unidirectional forward rate V_+ of an overall reaction is expressed, in the presence of a rate-determining step r , as

$$V_+ = v_{+r} / \nu(r), \quad (2.1)$$

where $\nu(r)$ and v_{+r} are the stoichiometric number and the forward rate respectively of step r .

Let step (1.4.N) be rate-determining and the repulsive adsorbate be nitrogen adatom, N(a). The $a^{\delta(a)}$ and a^I in (1.14) are now according to the premise

$$a^{\delta(a)} = a^{N(a)} \quad (2.2.a^{\delta})$$

and

$$a^I = (a^{N(a)})^2, \quad (2.2.a^I)$$

inasmuch as I of (1.4.N) consists of a pair of nitrogen adatoms. All steps other than the rate-determining one are in partial equilibria, so that $\mu^I = \mu^F$ for (1.4.NH₃), (1.4.NH₂), (1.4.NH), and (1.4.H), or, according to (1.3) and (1.4), $a^{NH_3} = a^{NH_2(a)} a^{H(a)}$, $a^{NH_2(a)} = a^{NH(a)} a^{H(a)}$, $a^{NH(a)} = a^{N(a)} a^{H(a)}$ and $a^{H_2} = (a^{H(a)})^2$, hence

$$a^{N(a)} = a^{NH_3} / (a^{H_2})^{3/2}. \quad (2.3)$$

We have from (1.14), (2.1), (2.2), and (2.3) assigning $n=2$ to (1.4.N)

$$V_+ = v_{+r} = \kappa \left(\frac{kT}{h} \right) N_1^* (1 - \theta_{\sigma(N)})^{2-r} \theta_{\sigma(N)}^r \left\{ \frac{a^{NH_3}}{(a^{H_2})^{3/2}} \right\}^{2-r} e^{\frac{s_0^* - \gamma s_0^{N(a)}}{R}} e^{-\frac{\epsilon_0^* - \gamma \epsilon_0^{N(a)}}{RT}}, \quad (2.4)$$

*) $A^{\delta(a)}$ is the surface area of adsorbent apportioned to one unit of adsorption, e.g. a constituent surface atom of adsorbent, which bonds an adatom; cf. J. HORIUTI and T. TOYA, This Journal 11, 84 (1963), §4.

where $\theta_{\sigma(N)}$ is given by (1.12) as

$$\theta_{\sigma(N)} / (1 - \theta_{\sigma(N)}) = a^{N(a)} e^{s_0^{N(a)}/R} e^{-\frac{\varepsilon_0^{N(a)} + u\theta_{\sigma(N)}}{RT}}$$

or, referring to (2.3), as

$$\theta_{\sigma(N)} / (1 - \theta_{\sigma(N)}) = \frac{a^{NH_3}}{(a^{H_2})^{3/2}} e^{s_0^{N(a)}/R} e^{-\frac{\varepsilon_0^{N(a)} + u\theta_{\sigma(N)}}{RT}}. \quad (2.5)$$

The absolute activity $a^{\delta(g)}$ of a gaseous molecule $\delta(g)$ is expressed as¹⁵⁾

$$a^{\delta(g)} = N^{\delta(g)} / Q^{\delta(g)}, \quad (2.6)$$

where $Q^{\delta(g)}$ is the partition function of $\delta(g)$ in unit volume and $N^{\delta(g)}$ its concentration. $Q^{\delta(g)}$ is expressed for molecules of appreciably high vibrational frequencies as ammonia, nitrogen, and hydrogen, with good approximation as

$$Q^{\delta(g)} = Q_0^{\delta(g)} \exp(-\varepsilon^{\delta(g)} / RT), \quad (2.7)$$

where

$$Q_0^{\delta(g)} = \frac{(2\pi m^{\delta(g)} kT)^{3/2}}{h^3} \frac{8\pi^2 I^{\delta(g)} kT}{s_m^{\delta(g)} h^2}, \quad (2.8.1)$$

if $\delta(g)$ is linear or diatomic and

$$Q_0^{\delta(g)} = \frac{(2\pi m^{\delta(g)} kT)^{3/2}}{h^3} \frac{8\pi^2 (2\pi I^{\delta(g)} kT)^{3/2}}{s_m^{\delta(g)} h^2} \quad (2.8.m)$$

if $\delta(g)$ is nonlinear; $m^{\delta(g)}$ is the mass of $\delta(g)$, $I^{\delta(g)}$ the moment of inertia of diatomic and linear molecules or the geometric mean of the three principal moments of inertia of nonlinear molecules, $s_m^{\delta(g)}$ the symmetry number, and $\varepsilon^{\delta(g)}$ its energy in the ground state. $N^{\delta(g)}$ in (2.6), on the other hand, is written in terms of partial pressure $P_{\delta(g)}$ (in atm) of $\delta(g)$ as

$$N^{\delta(g)} = (7.34 \times 10^{21} / T) P_{\delta(g)}, \quad (2.9)$$

Eq. (2.4) is now written according to (2.6), (2.7) and (2.9) as

$$V_+ = k_{N,N} \theta_{\sigma(N)}^r (1 - \theta_{\sigma(N)})^{2-r} \{P_{NH_3} / (P_{H_2})^{3/2}\}^{2-r}, * \quad (2.10)$$

where

*) The Temkin-Pyzhev equation has been derived on the basis of the assumption that the adsorption energy of sites freshly occupied is a linear function of coverage, which is formally in perfect agreement with (2.10), provided that the coverage of N(a) is practically independent of partial pressures of ammonia and hydrogen. See also, S. BRUNAUER, K. S. LOVE and R. G. KEENAN, J. Am. Chem. Soc., **64**, 751 (1942).

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$$k_{N,N} = \kappa \left(\frac{kT}{h} \right) N_1^* \left(\frac{T}{7.34 \times 10^{21}} \right)^{(2-\tau)/2} \left\{ \frac{(Q_0^{H_2})^{3/2}}{Q_0^{NH_3}} \right\}^{2-\tau} e^{-\frac{s_0^* - \tau s_0^{N(a)}}{R}} \times e^{-\frac{\varepsilon_0^* - 2\varepsilon_0^{N(a)} + (2-\tau)(\varepsilon_0^{N(a)} + \frac{3}{2}\varepsilon_{H_2} - \varepsilon_{NH_3})}{RT}} \quad (2.11)$$

Eq. (2.5) is transformed similarly as

$$\frac{\theta_{\sigma(N)}}{(1-\theta_{\sigma(N)})} = \frac{(Q_0^{H_2})^{3/2}}{Q_0^{NH_3}} \frac{P_{NH_3}}{(P_{H_2})^{3/2}} \left(\frac{T}{7.34 \times 10^{21}} \right)^{1/2} e^{s_0^{N(a)}/R} e^{-\frac{\varepsilon_0^{N(a)} + u\theta_{\sigma(N)} + \frac{3}{2}\varepsilon_{H_2} - \varepsilon_{NH_3}}{RT}} \quad (2.12)$$

Table I shows the rate equations similarly derived each from a combination of rate-determining step repulsive adsorbate $\delta(a)$ indicated respectively in the

TABLE I
The Rate-Determining Step and the Rate Equations

Rate-determining Step	Repulsive adsorbate	Notation of combination	Rate equation
(1. 4. NH ₃)	NH ₂ (a)	(I-NH ₂)	$k_{NH_3, NH_2} \theta_{\sigma(NH_2)}^r (1-\theta_{\sigma(NH_2)})^{1-\tau} P_{NH_3} \{1/P_{N_2} (P_{H_2})^2\}^{\tau/2}$
"	NH(a)	(I-NH)	$k_{NH_3, NH} \theta_{\sigma(NH)}^r (1-\theta_{\sigma(NH)})^{1-\tau} P_{NH_3} \{1/P_{N_2} P_{H_2}\}^{\tau/2}$
"	N(a)	(I-N)	$k_{NH_3, N} \theta_{\sigma(N)}^r (1-\theta_{\sigma(N)})^{1-\tau} P_{NH_3} (1/P_{N_2})^{\tau/2}$
"	H(a)	(I-H)	$k_{NH_3, H} \theta_{\sigma(H)}^r (1-\theta_{\sigma(H)})^{1-\tau} P_{NH_3} (1/P_{H_2})^{\tau/2}$
(1. 4. NH ₂)	NH ₂ (a)	(II-NH ₂)	$k_{NH_2, NH_2} \theta_{\sigma(NH_2)}^r (1-\theta_{\sigma(NH_2)})^{1-\tau} \{P_{NH_3}/(P_{H_2})^{0.5}\}^{1-\tau}$
"	NH(a)	(II-NH)	$k_{NH_2, NH} \theta_{\sigma(NH)}^r (1-\theta_{\sigma(NH)})^{1-\tau} \{P_{NH_3}/(P_{H_2})^{0.5}\} \times (1/P_{N_2} P_{H_2})^{\tau/2}$
"	N(a)	(II-N)	$k_{NH_2, N} \theta_{\sigma(N)}^r (1-\theta_{\sigma(N)})^{1-\tau} \{P_{NH_3}/(P_{H_2})^{0.5}\} (1/P_{N_2})^{\tau/2}$
"	H(a)	(II-H)	$k_{NH_2, H} \theta_{\sigma(H)}^r (1-\theta_{\sigma(H)})^{1-\tau} \{P_{NH_3}/(P_{H_2})^{0.5}\} (1/P_{H_2})^{\tau/2}$
(1. 4. NH)	NH ₂ (a)	(III-NH ₂)	$k_{NH, NH_2} \theta_{\sigma(NH_2)}^r (1-\theta_{\sigma(NH_2)})^{1-\tau} (P_{NH_3}/P_{N_2}) \times \{(P_{H_2})^{0.5}/P_{NH_3}\}^{\tau}$
"	NH(a)	(III-NH)	$k_{NH, NH} \theta_{\sigma(NH)}^r (1-\theta_{\sigma(NH)})^{1-\tau} (P_{NH_3}/P_{H_2})^{1-\tau}$
"	N(a)	(III-N)	$k_{NH, N} \theta_{\sigma(N)}^r (1-\theta_{\sigma(N)})^{1-\tau} (P_{NH_3}/P_{H_2}) (1/P_{N_2})^{\tau/2}$
"	H(a)	(III-H)	$k_{NH, H} \theta_{\sigma(H)}^r (1-\theta_{\sigma(H)})^{1-\tau} (P_{NH_3}/P_{H_2}) (1/P_{H_2})^{\tau/2}$
(1. 4. N)	NH ₂ (a)	(IV-NH ₂)	$k_{N, NH_2} \theta_{\sigma(NH_2)}^r (1-\theta_{\sigma(NH_2)})^{2-\tau} \{(P_{NH_3})^2/(P_{H_2})^3\} \times \{(P_{H_2})^{1/2}/P_{NH_3}\}^{\tau}$
"	NH(a)	(IV-NH)	$k_{N, NH} \theta_{\sigma(NH)}^r (1-\theta_{\sigma(NH)})^{2-\tau} \{(P_{NH_3})^2/(P_{H_2})^3\} (P_{H_2}/P_{NH_3})^{\tau}$
"	N(a)	(IV-N)	$k_{N, N} \theta_{\sigma(N)}^r (1-\theta_{\sigma(N)})^{2-\tau} \{(P_{NH_3})^2/(P_{H_2})^{1.5}\}^{2-\tau}$
"	H(a)	(IV-H)	$k_{N, H} \theta_{\sigma(H)}^r (1-\theta_{\sigma(H)})^{2-\tau} \{(P_{NH_3})^2/(P_{H_2})^3\} (1/P_{H_2})^{\tau/2}$
(1. 4. H)	NH ₂ (a)	(V-NH ₂)	$k_{H, NH_2} \theta_{\sigma(NH_2)}^r (1-\theta_{\sigma(NH_2)})^{2-\tau} \{(P_{NH_3})^2/P_{N_2}\}^{1/3} \times \{(1/P_{NH_3})^{2/3} (P_{N_2})^{1/6}\}^{\tau}$
"	NH(a)	(V-NH)	$k_{H, NH} \theta_{\sigma(NH)}^r (1-\theta_{\sigma(NH)})^{2-\tau} \{(P_{NH_3})^2/P_{N_2}\}^{1/3} \times \{(1/P_{NH_3})^{1/3} (P_{N_2})^{1/3}\}^{\tau}$
"	N(a)	(V-N)	$k_{H, N} \theta_{\sigma(N)}^r (1-\theta_{\sigma(N)})^{2-\tau} \{(P_{NH_3})^2/P_{N_2}\}^{1/3} (1/P_{N_2})^{\tau/2}$
"	H(a)	(V-H)	$k_{H, H} \theta_{\sigma(H)}^r (1-\theta_{\sigma(H)})^{2-\tau} \{(P_{NH_3})^2/P_{N_2}\}^{1/3} (1-\frac{1}{2}\tau)$

first and the second column.*)

3. The Mechanism of the Decomposition around 425°C

(i) The Order of Reaction

The order of reaction is derived from the rate equations in Table I. We have in case of (IV-N), for instance, the order of reaction with respect to ammonia, x , as

$$x = \left(\frac{\partial \ln V_+}{\partial \ln P_{\text{NH}_3}} \right)_{P_{\text{H}_2}, P_{\text{N}_2}, T} = \frac{\gamma - 2\theta_{\sigma(\text{N})}}{\theta_{\sigma(\text{N})}(1 - \theta_{\sigma(\text{N})})} \left(\frac{\partial \theta_{\sigma(\text{N})}}{\partial \ln P_{\text{NH}_3}} \right)_{P_{\text{H}_2}, P_{\text{N}_2}, T} + (2 - \gamma), \quad (3.1.a)$$

that to hydrogen, y , as

$$y = \left(\frac{\partial \ln V_+}{\partial \ln P_{\text{H}_2}} \right)_{P_{\text{NH}_3}, P_{\text{N}_2}, T} = \frac{\gamma - 2\theta_{\sigma(\text{N})}}{\theta_{\sigma(\text{N})}(1 - \theta_{\sigma(\text{N})})} \left(\frac{\partial \theta_{\sigma(\text{N})}}{\partial \ln P_{\text{H}_2}} \right)_{P_{\text{NH}_3}, P_{\text{N}_2}, T} - \frac{3}{2}(2 - \gamma), \quad (3.1.h)$$

or that to nitrogen, z , as

$$z = \left(\frac{\partial \ln V_+}{\partial \ln P_{\text{N}_2}} \right)_{P_{\text{NH}_3}, P_{\text{H}_2}, T} = 0; \quad (3.1.n)$$

derivatives of $\theta_{\sigma(\text{N})}$ comprised in the above equations are derived from (2.12) as,

$$\left(\frac{\partial \ln \theta_{\sigma(\text{N})}}{\partial \ln P_{\text{NH}_3}} \right)_{P_{\text{H}_2}, P_{\text{N}_2}, T} = \frac{\theta_{\sigma(\text{N})}(1 - \theta_{\sigma(\text{N})})}{\frac{u}{RT} \theta_{\sigma(\text{N})}(1 - \theta_{\sigma(\text{N})}) + 1} \quad (3.2.a)$$

and

$$\left(\frac{\partial \ln \theta_{\sigma(\text{N})}}{\partial \ln P_{\text{H}_2}} \right)_{P_{\text{NH}_3}, P_{\text{N}_2}, T} = -\frac{3}{2} \frac{\theta_{\sigma(\text{N})}(1 - \theta_{\sigma(\text{N})})}{\frac{u}{RT} \theta_{\sigma(\text{N})}(1 - \theta_{\sigma(\text{N})}) + 1}, \quad (3.2.h)$$

hence

$$x = \frac{\gamma - 2\theta_{\sigma(\text{N})}}{\frac{u}{RT} \theta_{\sigma(\text{N})}(1 - \theta_{\sigma(\text{N})}) + 1} + (2 - \gamma) \quad (3.3.a)$$

and

$$y = -\frac{3}{2} \left\{ \frac{\gamma - 2\theta_{\sigma(\text{N})}}{\frac{u}{RT} \theta_{\sigma(\text{N})}(1 - \theta_{\sigma(\text{N})}) + 1} + (2 - \gamma) \right\}. \quad (3.3.h)$$

The orders, x , y , and z , in other cases are similarly derived.

The observed values of x , y , and z were found to be 0.41, -0.64, and

*) It is assumed that $n=2$ for (1.4 N) and (1.4 H) and $n=1$ for other steps.

TABLE II
The Orders of Reaction

Notation of Combination *)	x	y	Relation between x and y
(II-NH ₂)	$(1-\gamma) + \frac{\gamma - \theta_{\sigma(\text{NH}_2)}}{\frac{u}{RT} \theta_{\sigma(\text{NH}_2)}(1 - \theta_{\sigma(\text{NH}_2)}) + 1}$	$\frac{1}{2}(\gamma - 1) - \frac{\frac{1}{2}(\gamma - \theta_{\sigma(\text{NH}_2)})}{\frac{u}{RT} \theta_{\sigma(\text{NH}_2)}(1 - \theta_{\sigma(\text{NH}_2)}) + 1}$	$y = -\frac{1}{2}x$
(III-NH ₂)	$(1-\gamma) + \frac{\gamma - \theta_{\sigma(\text{NH}_2)}}{\frac{u}{RT} \theta_{\sigma(\text{NH}_2)}(1 - \theta_{\sigma(\text{NH}_2)}) + 1}$	$\frac{1}{2}\gamma - 1 - \frac{\frac{1}{2}(\gamma - \theta_{\sigma(\text{NH}_2)})}{\frac{u}{RT} \theta_{\sigma(\text{NH}_2)}(1 - \theta_{\sigma(\text{NH}_2)}) + 1}$	$y = -\frac{1}{2}x - \frac{1}{2}$
(III-NH)	$(1-\gamma) + \frac{\gamma - \theta_{\sigma(\text{NH})}}{\frac{u}{RT} \theta_{\sigma(\text{NH})}(1 - \theta_{\sigma(\text{NH})}) + 1}$	$\gamma - 1 - \frac{\gamma - \theta_{\sigma(\text{NH})}}{\frac{u}{RT} \theta_{\sigma(\text{NH})}(1 - \theta_{\sigma(\text{NH})}) + 1}$	$y = -x$
(IV-NH ₂)	$(2-\gamma) + \frac{\gamma - 2\theta_{\sigma(\text{NH}_2)}}{\frac{u}{RT} \theta_{\sigma(\text{NH}_2)}(1 - \theta_{\sigma(\text{NH}_2)}) + 1}$	$\frac{1}{2}\gamma - 3 - \frac{\frac{1}{2}(\gamma - 2\theta_{\sigma(\text{NH}_2)})}{\frac{u}{RT} \theta_{\sigma(\text{NH}_2)}(1 - \theta_{\sigma(\text{NH}_2)}) + 1}$	$y = -\frac{1}{2}x - 2$
(IV-NH)	$(2-\gamma) + \frac{\gamma - 2\theta_{\sigma(\text{NH})}}{\frac{u}{RT} \theta_{\sigma(\text{NH})}(1 - \theta_{\sigma(\text{NH})}) + 1}$	$\gamma - 3 - \frac{\gamma - 2\theta_{\sigma(\text{NH})}}{\frac{u}{RT} \theta_{\sigma(\text{NH})}(1 - \theta_{\sigma(\text{NH})}) + 1}$	$y = -x - 1$
(IV-N)	$(2-\gamma) + \frac{\gamma - 2\theta_{\sigma(\text{N})}}{\frac{u}{RT} \theta_{\sigma(\text{N})}(1 - \theta_{\sigma(\text{N})}) + 1}$	$\frac{3}{2} \left\{ \gamma - 2 - \frac{\gamma - 2\theta_{\sigma(\text{N})}}{\frac{u}{RT} \theta_{\sigma(\text{N})}(1 - \theta_{\sigma(\text{N})}) + 1} \right\}$	$y = -\frac{3}{2}x$

*) See Table I.

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0 respectively independent of the partial pressures of ammonia, hydrogen, and nitrogen around 425°C over the commercial iron catalyst reduced at 600°C,¹¹⁻¹⁴⁾ which shows that terms containing the surface coverage and its pressure dependence, such as the first term on the right-hand side of (3.1), are kept practically constant under the present experimental conditions. Rate equations other than those in case of (II-NH₂), (III-NH₂), (III-NH), (IV-NH₂), (IV-NH) and (IV-N) are excluded, since they lead to the conclusion that $x=1$ and $y=2$ or 0. The included rate equations give, however theoretical relations between x and y as shown in Table II, of which only those in case of (III-NH₂) and of (IV-N) fit in with the observed result.

The rates of (1.4.N) and of the formation of nitrogen adatoms from ammonia through the steps (1.4.NH₃), (1.4.NH₂), and (1.4.NH) have recently been determined^{22,23)} from by simultaneous observations of ammonia decomposition rate and isotopic exchange rate between nitrogen and ammonia at 550 mm Hg and at 305 and 340°C. It was thus found that (1.4.N) was much slower than the formation of nitrogen adatom from ammonia in agreement with the results that the stoichiometric number of the rate-determining step was unity, as seen with reference to (1.4).^{22,23)}*) We hence conclude that the rate of decomposition is determined by (1.4.N) around 425°C. This conclusion is supported, moreover, by the following estimates of the activation heat of decomposition and of the number of sites of the critical complex per unit area.

(ii) Estimate of $\theta_{\sigma(N)}$

The $\theta_{\sigma(N)}$ is expressed in terms of the equilibrium constant, K_p , of ammonia synthesis reaction $N_2 + 3H_2 = 2NH_3$ as follows. In equilibrium, we have $(a_e^{NH_3})^2 = a_e^{N_2}(a_e^{H_2})^3$ since $a_e^{NH_3}$ etc. are reciprocal Boltzmann factors of the relevant chemical potentials respectively, hence according to (2.6), (2.7) and (2.9)

$$K_p = \frac{(P_{e,NH_3})^2}{P_{e,N_2}(P_{e,H_2})^3} = \frac{(Q_0^{NH_3})^2}{Q_0^{N_2}(Q_0^{H_2})^3} \left(\frac{7.34 \times 10^{21}}{T} \right)^2 e^{-\frac{2\epsilon^{NH_3} - \epsilon^{N_2} - 3\epsilon^{H_2}}{RT}}, \quad (3.4)$$

*) ENOMOTO and HORIUTI⁵⁾ determined the stoichiometric number of rate-determining step of ammonia synthesis reaction over commercial doubly promoted iron catalyst to be 2, in contrast to TANAKA's result.^{22,23)} The activity of their catalyst⁵⁾ was, however, much less than that of TANAKA. HORIUTI and TOYOSHIMA^{6,7)} and HORIUTI and TAKEZAWA²⁴⁾ determined pressure dependences of the rate of ammonia decomposition and synthesis in consistence with the results of ENOMOTO and HORIUTI⁵⁾, but their catalyst^{6,7,24)} was much less active than and the kinetics observed was quite different from the present one. The mechanism of ammonia decomposition or synthesis may thus vary with the activity of catalyst.^{25,26)} The activity of the present catalyst was close to that of TANAKA, hence his results appear relevant to the present discussion.

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where suffix *e* indicates particular values in equilibrium.

The surface coverage, $\theta_{\sigma(N)}$, of nitrogen adatoms in course of decomposition is now given by eliminating $(Q_0^{H_2})^{3/2}/Q_0^{NH_3}$ from (2.12) and (3.4) as

$$\frac{\theta_{\sigma(N)}}{1-\theta_{\sigma(N)}} = \left(\frac{K_p}{Q_0^{N_2}}\right)^{-1/2} \frac{P_{NH_3}}{(P_{H_2})^{3/2}} \left(\frac{7.34 \times 10^{21}}{T}\right) e^{s_0^{N(a)}/R} e^{-\frac{\varepsilon_0^{N(a)} + u\theta_{\sigma(N)} - \frac{1}{2}\varepsilon^{N_2}}{RT}}. \quad (3.5)$$

The last exponential factor (3.5) is determined as follows from the experimental results of nitrogen adsorption on the catalyst. We have from (1.12), (2.6) and (2.7), noting that $a^{N(a)} = (a^{N_2})^{1/2}$ in case of adsorption equilibrium,

$$\left(\frac{\theta_{\sigma(N)}}{1-\theta_{\sigma(N)}}\right)^2 = \left(\frac{N^{N_2}}{Q_0^{N_2}}\right) e^{2s_0^{N(a)}/R} e^{-\frac{2\varepsilon^{N(a)} + u\theta_{\sigma(N)} - \varepsilon^{N_2}}{RT}}, \quad (3.6.N)$$

or in terms of partial pressure P_{N_2} of nitrogen according to (2.9)

$$\left(\frac{\theta_{\sigma(N)}}{1-\theta_{\sigma(N)}}\right)^2 = \left(\frac{P_{N_2}}{Q_0^{N_2}}\right) \left(\frac{7.34 \times 10^{21}}{T}\right) e^{2s_0^{N(a)}/R} e^{-\frac{2\varepsilon_0^{N(a)} + u\theta_{\sigma(N)} - \varepsilon^{N_2}}{RT}}. \quad (3.6.P)$$

The isosteric heat of adsorption, q , is derived from (3.6.P) with reference to (1.16) and (2.8.1) both for immobile and mobile nitrogen adatoms assuming that u is independent of temperature, as

$$q = RT^2 \left(\frac{\partial \ln P_{N_2}}{\partial T}\right)_{\theta_{\sigma(N)}} = q_0 - 2u\theta_{\sigma(N)}, \quad (3.7)$$

where

$$q_0 = \frac{7}{2} RT - 2T^2 \left(\frac{\partial s_0^{N(a)}}{\partial T}\right)_{\theta_{\sigma(N)}} - (2\varepsilon_0^{N(a)} - \varepsilon^{N_2}), \quad (3.8)$$

and

$$\left(\frac{\partial s_0^{N(a)}}{\partial T}\right)_{\theta_{\sigma(N)}} = 0 \quad (\text{immobile adsorption}) \quad (3.9.i)$$

or

$$\left(\frac{\partial s_0^{N(a)}}{\partial T}\right)_{\theta_{\sigma(N)}} = R/T. \quad (\text{mobile adsorption}) \quad (3.9.m)$$

Parameters, q_0 and u in (3.7) are determined on the base of observation of KWAN,²⁷⁾ who found that the heat of adsorption of nitrogen on doubly promoted iron catalyst decreased from 42 to 15 kcal/mole with increase of surface coverage $\theta_{\sigma(N)}$ from 0.08 to 0.4, as

$$q_0 = 48.7 \text{ kcal/mole} \quad (3.10)$$

and

$$u = 42 \text{ kcal/mole.} \quad (3.11)$$

The $\theta_{\sigma(N)}$ is now determined to be 0.3 or 0.51 in case of immobile and mobile adsorption*) respectively by solving (3.6.P) at 425°C, $P_{N_2}=0.1$ and $P_{H_2}=0.4$ atm in accordance with our experimental condition evaluating $2\epsilon_0^{N(a)}-\epsilon^{N_2}$ by (3.8) and (3.10), referring to (3.11) and (1.16) and assuming $A^{\delta(a)}=10A^{2,21}$ **) .

The γ -values are calculated by (3.3) from the observed orders of reaction with respect to ammonia and hydrogen, $x=0.41$ and $y=-0.64$, and the surface coverage just obtained. The numerical values of γ are thus determined to be 1.75 and 1.63 for immobile and mobile***) adsorption of nitrogen atoms respectively.

(iii) The Activation Heat

The activation heat E , at constant partial pressures of ammonia and hydrogen is deduced from (2.10) and (2.11) as,

$$E = RT^2(\partial \ln V_+/\partial T)_{P_{NH_3}, P_{H_2}} = (2-\gamma)RT^2 \left\{ \frac{\partial \ln (Q_0^{H_2})^{3/2}/Q_0^{NH_3}}{\partial T} \right\}_{P_{NH_3}, P_{H_2}} \\ + T^2 \left\{ \frac{\partial (s_0^* - \gamma s_0^{N(a)})}{\partial T} \right\}_{P_{NH_3}, P_{H_2}} + \frac{\gamma - 2\theta_{\sigma(N)}}{\theta_{\sigma(N)}(1-\theta_{\sigma(N)})} RT^2 \left(\frac{\partial \theta_{\sigma(N)}}{\partial T} \right)_{P_{NH_3}, P_{H_2}} \\ + \frac{4-\gamma}{2} RT + E^* , \quad (3.12)$$

*) Numerical values used in the present calculation are the equilibrium constant, $K_p = 10^{-4.014}$ of the ammonia synthesis reaction $N_2 + 3H_2 = 2NH_3$,²⁸⁾ and the moment of inertia of nitrogen molecule, $I^{N_2} = 13.9 \times 10^{-40}$ g. cm².

**) The value of $A^{\delta(a)}$ was taken approximately the same as that of $A^{\delta(a)}$ on nickel.¹⁶⁾

***) The order of reaction is calculated by (3.3) using the values of just determined and u in (3.11) as a function of the surface coverage $\theta_{\sigma(N)}$. The values of x and y thus obtained are listed below for immobile and mobile adsorption of nitrogen, which shows how the value of γ reproduce the values of $\theta_{\sigma(N)}$, x and y from which γ is to be determined.

Surface coverage $\theta_{\sigma(N)}$	x		y	
	(immobile ads.)	(mobile ads.)	(immobile ads.)	(mobile ads.)
0	2	2	-3	-3
0.1	0.67	0.72	-1.00	-1.08
0.2	0.48	0.54	-0.72	-0.81
0.3	0.41	0.47	-0.62	-0.71
0.4	0.37	0.43	-0.55	-0.65
0.5	0.34	0.41	-0.51	-0.62
0.6	0.32	0.38	-0.48	-0.57
0.7	0.30	0.36	-0.45	-0.54
0.8	0.28	0.33	-0.42	-0.50
0.9	0.24	0.29	-0.36	-0.44
1.0	0	0	0	0

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where

$$E^* = (\varepsilon_0^* - 2\varepsilon_0^{N(a)}) + (2-\gamma) \left(\varepsilon_0^{N(a)} + \frac{3}{2} \varepsilon^{H_2} - \varepsilon^{NH_3} \right). \quad (3.13)$$

The derivatives in the first three terms of (3.12) are expressed according to (1.16), (2.8) and (2.12), assuming the same dependence of s_0^* on temperature as that of $s_0^{N(a)}$ in the respective cases of immobile and mobile adsorption, as

$$\left\{ \frac{\partial \ln (Q_0^{H_2})^{3/2} / Q_0^{NH_3}}{\partial T} \right\}_{P_{NH_3}, P_{H_2}} = \frac{3}{4} \frac{1}{T}, \quad (3.14)$$

$$\left\{ \frac{\partial (s_0^* - \gamma s_0^{N(a)})}{\partial T} \right\}_{P_{NH_3}, P_{H_2}} = 0, \quad (\text{immobile adatoms}) \quad (3.15. i)$$

or

$$\left\{ \frac{\partial (s_0^* - \gamma s_0^{N(a)})}{\partial T} \right\}_{P_{NH_3}, P_{H_2}} = \frac{1-\gamma}{T} R \quad (\text{mobile adatoms}) \quad (3.15. m)$$

and

$$\left(\frac{\partial \theta_{\sigma(N)}}{\partial T} \right)_{P_{NH_3}, P_{H_2}} = \frac{\theta_{\sigma(N)}(1-\theta_{\sigma(N)})}{\frac{u}{RT} \theta_{\sigma(N)}(1-\theta_{\sigma(N)}) + 1} \left(\frac{5}{4T} + \frac{\varepsilon_0^{N(a)} + u\theta_{\sigma(N)} + \frac{3}{2}\varepsilon^{H_2} - \varepsilon^{NH_3}}{RT^2} \right) \quad (\text{immobile adatoms}) \quad (3.16. i)$$

or

$$\left(\frac{\partial \theta_{\sigma(N)}}{\partial T} \right)_{P_{NH_3}, P_{H_2}} = \frac{\theta_{\sigma(N)}(1-\theta_{\sigma(N)})}{\frac{u}{RT} \theta_{\sigma(N)}(1-\theta_{\sigma(N)}) + 1} \left(\frac{9}{4T} + \frac{\varepsilon_0^{N(a)} + u\theta_{\sigma(N)} + \frac{3}{2}\varepsilon^{H_2} - \varepsilon^{NH_3}}{RT^2} \right). \quad (\text{mobile adatoms}) \quad (3.16. m)$$

We have thus from (3.12), (3.13), (3.14), (3.15), and (3.16)

$$E = E_d^0 + \frac{(2-\gamma)}{2} (Q - q_0) + \frac{\gamma - 2\theta_{\sigma(N)}}{\frac{u}{RT} \theta_{\sigma(N)}(1-\theta_{\sigma(N)}) + 1} \left\{ u\theta_{\sigma(N)} + \frac{1}{2} (Q - q_0) \right\}, \quad (3.17)$$

where

$$E_d^0 = \varepsilon_0^* - 2\varepsilon_0^{N(a)} + RT \quad (\text{immobile adsorption}) \quad (3.18. i)$$

or

$$E_d^0 = \varepsilon_0^* - 2\varepsilon_0^{N(a)} \quad (\text{mobile adsorption}) \quad (3.18. m)$$

is the activation heat of desorption of nitrogen adatoms at $\theta_{\sigma(N)} = 0^*$ and

*) See Appendix.

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$$Q = \varepsilon^{N_2} + 3\varepsilon^{H_2} - 2\varepsilon^{NH_3} + 6RT \quad (3.19)$$

is the heat toning at constant pressure of ammonia synthesis, $N_2 + 3H_2 = 2NH_3$.

The r and $\theta_{\sigma(N)}$ in (3.17) have been evaluated above in (ii) to be 1.75 and 0.3 or 1.63 and 0.51, for the immobile adsorption or mobile adsorption respectively, while E_a^0 and Q in the same equation observed to be $55^{*(27)}$ and 25 kcal/mole respectively. The activation heat E is hence calculated to be 53 kcal/mole, for both immobile and mobile adsorptions of nitrogen respectively, which is in satisfactory agreement with the observed value, $E=50.5$ kcal/mole.

(iv) Number of Sites of Critical Complex

The number of sites per unit area, N_1^* , of critical complex of rate-determining step is determined statistical-mechanically from experimental results as follows. We have from (2.10) and (2.11)

$$\begin{aligned} \log N_1^* = & \log V_+ - \log \kappa \left(\frac{kT}{h} \right) - \log \theta_{\sigma(N)}^r (1 - \theta_{\sigma(N)})^{2-r} \\ & - (2-r) \log \frac{P_{NH_3}}{(P_{H_2})^{3/2}} \left(\frac{T}{7.34 \times 10^{21}} \right)^{1/2} \frac{(Q_0^{H_2})^{3/2}}{Q^{NH_3}} - \frac{s_0^* - \gamma s_0^{N(a)}}{2.3R} \\ & + \frac{\varepsilon_0^* - 2\varepsilon_0^{N(a)} + (2-r)(\varepsilon_0^{N(a)} + \frac{3}{2}\varepsilon^{H_2} - \varepsilon^{NH_3})}{2.3RT} \end{aligned} \quad (3.20)$$

Eliminating $\varepsilon_0^* - 2\varepsilon_0^{N(a)}$, E_a^0 , Q and q_0 from the last term in (3.20), (3.17), (3.18), (3.19) and (3.8), we have

$$\begin{aligned} \text{Last term} = & \frac{E - \frac{1}{4}(14-5r)RT - (1-r)T^2(\partial s_0^{N(a)}/\partial T)_{\sigma(N)}}{2.3RT} \\ & - \frac{(\gamma - 2\theta_{\sigma(N)}) \left(u\theta_{\sigma(N)} + \frac{Q - q_0}{2} \right) \left\{ \frac{u\theta_{\sigma(N)}(1 - \theta_{\sigma(N)})}{RT} + 1 \right\}}{2.3RT} \end{aligned} \quad (3.21)$$

N_1^* is worked out to be $10^{15.9}$ or 10^{16} cm^{-2} for the immobile or mobile adsorption respectively by (3.20) and (3.21) at $T=698^\circ\text{K}$, $P_{N_2}=0.1$ and $P_{H_2}=0.4$ atm on the base of fundamental data shown below, assuming κ to be unity.

	$\log V_+$	$\theta_{\sigma(N)}$	r	$A^{N(a)}$	$s_0^* = s_0^{N(a)}$
Immobile ads.	12.43	0.30	1.75	0	0
Mobile ads.	12.43	0.51	1.63	$10 A^2$ **)	0.67

*) The E_a^0 is evaluated as the sum of the heat of adsorption, as given by (3.10), and the observed activation heat of the adsorption²⁷⁾ of nitrogen respectively at $\theta_{\sigma(N)}=0$.

***) Cf. footnote *) on p. 115.

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The calculated value of N_1^* is in fairly good agreement with the crystallographic number of lattice points, 10^{15} cm^{-2} , which provides another support to the conclusion of (IV-N), whether the sites are immobile or mobile.

We thus conclude that the rate-determining step is the desorption of nitrogen adatoms around 425°C in conformity with TANAKA'S^{22,23)} conclusion that the stoichiometric number of the rate-determining step is unity.

4. The Mechanism of the Decomposition around 480°C

The orders of reaction with respect to ammonia, hydrogen and nitrogen were found to be 0.7, -0.3 and almost zero¹¹⁻¹⁴⁾ respectively. This result indicates that (1.4.N) is no longer rate-determining at 480°C . It is shown, on the other hand, similarly as in the case of 3.(i) that (II-NH₂) only fits in with the experimental result.

It follows that the rate-determining step shifts from the desorption of nitrogen adatoms to the dehydrogenation of adsorbed amino group with rise of the temperature.

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Appendix

Activation Heat of Nitrogen Desorption

The activation heat of nitrogen desorption, E_d is developed according to (2.1) and (1.14) assuming that $\kappa=1$, and $n=2$, and noting that repulsive adsorbate in this case is N(a) and $a^I=(a^{N(a)})^2$, as

$$E_d = RT^2 \left(\frac{\partial \ln V_{des}}{\partial T} \right)_{\theta_{\sigma(N)}} = (\varepsilon_0^* - \gamma \varepsilon_0^{N(a)}) + RT + T^2 \left\{ \frac{\partial (s_0^* - \gamma s_0^{N(a)})}{\partial T} \right\}_{\theta_{\sigma(N)}} + RT^2 \left\{ \frac{\partial \ln (a^{N(a)})^{2-r}}{\partial T} \right\}_{\theta_{\sigma(N)}}; \quad (i)$$

the fourth term in the third member is transformed by (1.12) as

$$RT^2 \left\{ \frac{\partial \ln (a^{N(a)})^{2-r}}{\partial T} \right\}_{\theta_{\sigma(N)}} = -(2-r) \left\{ T^2 \left(\frac{\partial s_0^{N(a)}}{\partial T} \right)_{\theta_{\sigma(N)}} + \varepsilon_0^{N(a)} + u\theta_{\sigma(N)} \right\}. \quad (ii)$$

We have hence, identifying s_0^* with $s_0^{N(a)}$

$$E_d = \varepsilon_0^* - 2\varepsilon_0^{N(a)} - T^2 (\partial s_0^{N(a)} / \partial T)_{\theta_{\sigma(N)}} - (2-r)u\theta + RT, \quad (iii)$$

where the third term assumes the value, zero or $-RT$, according to (1.16) for the immobile or mobile adsorption respectively.

E_d is particularly at $\theta_{\sigma(N)}=0$

$$E_d^0 = \varepsilon_0^* - 2\varepsilon_0^{N(a)} + RT \quad (\text{immobile ads.}) \quad (iv-i)$$

or

$$E_d^0 = \varepsilon_0^* - 2\varepsilon_0^{N(a)}. \quad (\text{mobile ads.}) \quad (iv-m)$$