A Kinetic Structure of Ammonia Synthesis

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The adsorption measurements during surface catalysis[1] have been extended to the study of the reactivity of chemisorbed species on the catalyst surface as a function of the pressures and coverages of such species as reactants, products and intermediates.[2] Accordingly, the mechanism of the overall reaction can be elucidated by studying each step in the overall reaction.

The ammonia synthesis on a doubly promoted iron catalyst has been treated by the new approach, and the chemisorption of nitrogen and its desorption, the reaction between the chemisorbed nitrogen and hydrogen to form ammonia have been separately studied under the reaction conditions.[2-4] The rates of the three steps ($\overrightarrow{V}_1$, $\overleftarrow{V}_1$ and $\overrightarrow{V}_2$, respectively) are expressed in the following manner according to the experimental results:

$$\overrightarrow{V}_1 = AP_{N_2} \exp(-\gamma x) \tag{1}$$

$$\overleftarrow{V}_1 = B \exp(\beta x) \tag{2}$$

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[1] K. Tamaru, This Bulletin, 31, 666 (1958).

[2] K. Tamaru, *Catalyst* (*Shokubai*), 4, 30 (1962).

[3] K. Tamaru, *Trans. Faraday Soc.*, 59, 979 (1963).

[4] K. Tamaru, This Bulletin, 37, 771 (1964).

$$\overrightarrow{V}_2 = CP_{H_2}\ \exp(\alpha x) \tag{3}$$

where x is the amount of nitrogen chemisorbed A, B, C, α, β, γ, are constants, and P_N and P_H are the pressures of nitrogen and hydrogen respectively.

If we postulate that the backward reaction of the latter step ($\overleftarrow{V}_2$) is first order as to ammonia, as has been reported in the case of a tungsten catalyst, $\overleftarrow{V}_2$ should conform to the following equation from the equilibrium conditions:

$$\overleftarrow{V}_2 = D(P_{NH3}/\sqrt{P_{H_2}})\exp(-\delta x) \tag{4}$$

where $B/A = C^2/(D^2K_p)$, $\alpha+\beta = 2(\gamma+\delta)$, and K_p is the equilibrium constant of the reaction, $N_2 + 3H_2 = 2NH_3$.

The $\overleftarrow{V}_1/\overrightarrow{V}_2$ ratio can be taken as a criterion to identify the rate-determining step of the overall reaction; if it is much larger than unity, the latter step is rate-determining, while if it is much smaller than unity, the former step is.

$$\overleftarrow{V}_1/\overrightarrow{V}_2 = (B/C)\exp[(\beta-\gamma)x]/P_{H_2} \tag{5}$$

The experimental results revealed that β is approximately equal to γ and that the activation energy for $\overleftarrow{V}_1$, which is the sum of that for $\overrightarrow{V}_1$ and the heat of adsorption of nitrogen, is markedly larger than that for $\overrightarrow{V}_2$. Accordingly, at a higher temperature and a lower pressure of hydrogen, the latter step is likely to be rate-determining.

If the steady-state approximation is applied, the kinetic expression of the overall reaction can be derived in the following way:

$$\overrightarrow{V}_1 + \overleftarrow{V}_2 = \overleftarrow{V}_1 + \overrightarrow{V}_2$$

$$AP_{N_2}\exp(-\alpha x) + D(P_{NH_3}/\sqrt{P_{H_2}})\exp(-\delta x)$$
$$= B\ \exp(\beta x) + CP_{H_2}\exp(\gamma x)$$

$$\exp[(\alpha+\beta)x/2] = \frac{1}{2(B+CP_{H_2})}$$
$$\left[D\frac{P_{NH_3}}{\sqrt{p_{H_2}}} + \sqrt{D^2\frac{P^2_{NH_3}}{p_{H_2}} + 4AP_{N_2}(B+CP_{H_2})}\right] \tag{6}$$

$$\text{Overall rate } (V_0) = \overrightarrow{V}_1 - \overleftarrow{V}_1$$
$$= AP_{N_2}\exp(-\alpha x) - B\ \exp(\beta x) \tag{7}$$

Equation 6 gives the nitrogen coverage under given reaction conditions, while Eq. 7 gives the overall reaction rate at the nitrogen coverage.

If the former step is rate-determining, the Temkin-Pyzhev treatment[5)] is exactly applicable as follows:

$$V_0 = A^{\frac{\beta}{\alpha+\beta}}(K_pB)^{\frac{\alpha}{\alpha+\beta}}P_{N_2}(P^3{}_{H_2}/P^2{}_{NH})^{\frac{\alpha}{\alpha+\beta}}$$
$$-(A/K_p)^{\frac{\beta}{\alpha+\beta}}B^{\frac{\alpha}{\alpha+\beta}}(P^2{}_{NH3}/P^3{}_{H_2})^{\frac{\beta}{\alpha+\beta}} \tag{8}$$

From the experimental results, $\alpha/(\alpha+\beta) = 0.6$ was obtained, which conforms to the value hitherto obtained kinetically.

If the synthesis reaction proceeds in the presence of a negligible amount of ammonia, V_0 can be expressed as follows, putting P_{NH_3} as zero in Eqs. 6 and 7:

$$V_0 = AP_{N_2}[(AP_{N_2}/(B+CP_{H_2})]^{\frac{-\alpha}{\alpha+\beta}}$$
$$-B[AP_{N_2}/(B+CP_{H_2})]^{\frac{\beta}{\alpha+\beta}} \tag{9}$$

The orders of the forward reaction as to nitrogen and hydrogen are, accordingly, $\beta/(\alpha+\beta)$ and $\alpha/(\alpha+\beta)$ respectively, provided $CP_{H_2} \gg B$. It is of great interest to note that Temkin et al.[6)] recently reported that the ammonia synthesis in the presence of a negligible amount of ammonia is half-order as to both nitrogen and hydrogen. On the basis of this fact, they suggested that the hydrogenation step of the chemisorbed nitrogen participates in the rate-determining step of the overall reaction. Equation 9 reasonably agrees with the observed kinetics, which seemingly supports the validity of the general kinetic treatment of the overall reaction on the basis of the kinetics of each component step of the overall reaction.

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[5)] M. I. Temkin and V. Pyzhev, *Acta Physicochim.*, **12**, 327 (1940).

[6)] M. I. Temikin, N. M. Morozov and E. N. Shapatina, *Kinetics and Catalysis* (*U. S. S. R*), **4**, 260, 565 (1963).