

On the Rate of Hydrogenation of Preadsorbed Nitrogen

The rate of hydrogenation of preadsorbed nitrogen has been measured by several workers to elucidate relative importance of the hydrogenation step in the ammonia synthesis reaction (1-5). The commonly adopted method to evaluate the rate of hydrogenation is based on determination of the amount of ammonia in the effluent hydrogen from the catalyst bed containing preadsorbed nitrogen. The apparent rate of hydrogenation obtained on Mo_2N was previously shown to be proportional to the flow rate of hydrogen (4), demonstrating that the ammonia in the effluent hydrogen was in equilibrium with the adsorbed nitrogen. In conformity with this, the observed deuterium isotope effect on the "rate" of hydrogenation was in agreement with the theoretical value expected from the equilibrium constants ratio (4). Thus the analogous result on a doubly promoted iron catalyst obtained by Tamaru (1) was similarly explained (6). Takezawa (5) later carried out the hydrogenation experiments on a doubly promoted iron employing a non-recycling flow system instead of the circulating system adopted in the foregoing experiments, thus making it possible to apply a much higher flow rate of hydrogen. In this way Takezawa could determine the effect of flow rate on the "rate" of hydrogenation of preadsorbed nitrogen, although the effect of flow rate was not fully taken into account in his interpretation of the results. In this respect, an equation which correlates the observed rate with the flow rate is derived to elucidate the nature of observed rate as well as the associated isotope effect and activation energy.

Since the observed rate of hydrogenation (V_h) of preadsorbed nitrogen is measured by the amount of ammonia in the effluent

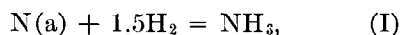
stream of hydrogen, it can be expressed by

$$V_h = C_A F, \quad (1)$$

where C_A and F denote the concentration of ammonia in the effluent and the flow rate of hydrogen, respectively. However, it should be recalled that the Eq. (1) is only valid for the initial rate. If the rate of hydrogenation depends on C_A , i.e., on F , the true rate, V_s , corresponding to C_A is given by $dC_A/d(1/F)$ at C_A so that the ratio $V_h/V_s = f$ is generally larger than unity, while it approaches unity as F increases. Since V_s is given by the difference between forward and backward rates, V_+ and V_- , respectively, it follows

$$\begin{aligned} C_A F &= f(V_+ - V_-) \\ &= fV_+(1 - C_A/K_A C_{\text{H}_2}^{1.5} A_N), \end{aligned} \quad (2)$$

where K_A denotes the equilibrium constant for the reaction,



with A_N being a function of amount of preadsorbed nitrogen. Thus by eliminating C_A from Eqs. (1) and (2), V_h is given by

$$V_h = fV_+ / (1 + fV_+ / FK_A C_{\text{H}_2}^{1.5} A_N). \quad (3)$$

It is evident that the measured value of V_h gives V_+ only when V_+/F is small enough, with f being unity. If V_+/F is large, on the other hand, V_h is approximated to

$$V_h = FK_A C_{\text{H}_2}^{1.5} A_N. \quad (4)$$

It is clear that the physical meaning of V_h depends on the magnitude of F relative to V_+ . The dependence of V_h on F is given by powers,

$$V_h \propto (fV_+)^n (FK_A C_{\text{H}_2}^{1.5} A_N)^{1-n}, \quad (5)$$

as an approximation from Eq. (3). The power n varies from unity to zero as V_+/F ,

forward rate over the flow rate, increases, giving Eq. (4) for $n = 0$.

It was previously shown that the observed rate of hydrogenation was in conformity with Eq. (4) with respect to dependences on F and K_A on Mo_2N catalyst (4) and hydrogen pressure (6) on a doubly promoted iron, demonstrating that the observed value of V_h by no means represents V_+ . It is clear that the flow rate was too small to measure the value of V_+ . According to Eq. (3) or (5), however, the situation would vary as temperature decreases, because V_+ is expected to decrease as temperature decreases resulting in an increase in the value of n . Since the deuterium isotope effect is determined by $V_+^n K_A^{1-n}$, the increase in n should give rise to a less pronounced isotope effect. The inverse isotope effect expected for K_A is decreased not only by the factor K_A^{1-n} but also by the factor V_+^n , the deuterium isotope effect on which is expected to be normal. Indeed, this is borne out by the results obtained by Tamaru (1) as well as by Takezawa (5) as follows:

Temp (°C):	180	250	320	162
			(1)	(5)
$(V_h)_D/(V_h)_H$	2.7	4.0	4.0	1.35
$(K_{AD}/K_{AH})_{\text{calc}}$	8.1	5.5	4.0	9.2

In this way the unusual decrease in the extent of isotope effect with decrease in temperature is now reasonable on the basis of Eq. (3).

Working with a flow reactor, Takezawa (5) could observe the dependence of V_h on F on a doubly promoted iron and obtained an n value of 0.25 at 162°C for the nitrogen preadsorbed at low temperatures near 200°C. The observed value of isotope effect $(V_h)_D/(V_h)_H = 1.35$ is too small as compared with the theoretical value of $[(K_A)_D/(K_A)_H]^{0.75} = 5.3$ at 162°C even when the cancellation by V_+^n is taken into consideration. In this sense the agreement with Eq. (5) is only qualitative. However, when the nitrogen was preadsorbed at high temperatures above 400°C, V_h was in-

dependent of F disclosing $n = 1$ and a normal isotope effect $[(V_h)_D/(V_h)_H = 1.25]$ was observed at 162°C, as expected from Eq. (5). Thus the significant difference in isotope effect caused by the difference in the adsorption temperature is very likely traced back to a large difference in the value of V_+ .

The nature of activation energy associated with V_h is also clear from Eq. (5). If the experimental condition corresponds to $n = 0$ as is likely the case for Tamaru's experiment (1), the activation energy stems from K_A instead of V_+ . Indeed, Tamaru obtained a value of 3.2 kcal/mol, an unusually low value as an activation energy for the hydrogenation. Since the heat effect on K_A , the heat of reaction for Eq. (1), is equal to the difference between the heat of adsorption of 0.5 mol of N_2 and the heat of formation of ammonia, the small value is not unusual.

In conclusion, the apparent rate of hydrogenation of adsorbed nitrogen significantly depends upon the flow rate of hydrogen. The rate obtained without considering the effect of flow rate is only a part of the rate of hydrogenation. This would not be the case for hydrogenation of adsorbed oxygen because K_A is much larger for oxygen than for nitrogen, making the reaction condition of $n = 1$ more probable.

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Received June 21, 1976; revised September 15, 1976