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Kinetics and Isotope Effect of Ammonia Synthesis Over a Singly-Promoted Iron Catalyst

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The kinetics and deuterium isotope effect of the ammonia synthesis reaction over a singly-promoted iron catalyst have been studied at 305°C under reduced pressures. The kinetic data as well as the isotope effect are essentially the same as those on the unpromoted iron previously reported. This result confirms that the potash promoter is more important in the mechanism of ammonia synthesis.

The mechanism and isotope effect of ammonia synthesis was previously studied on a doubly-promoted iron catalyst (*1*) and on an unpromoted iron catalyst (*2*). The difference in kinetics found over these two catalysts can be ascribed to the difference in the main adsorbed species, that is, N on the unpromoted iron and NH on the doubly-promoted iron, which seems to be caused by the potash promoter in the doubly-promoted iron. If this is the case, the singly-promoted iron (Fe–Al_2O_3) should behave like the unpromoted catalyst. This prediction has been tested in the similar manner as previously reported. The cause of the inverse deuterium isotope effect is again examined. The isotopic work on the singly-promoted iron has been requested elsewhere (*3*).

Experimental Methods

A singly-promoted iron of 2.2 % wt Al_2O_3 was obtained from the Government Chemical Industrial Research Institute, Tokyo. The catalyst was crushed to 8 to 10 mesh grains. The amount of the catalyst used was 2.53 g. The catalyst was reduced by circulating hydrogen at 400°C for 192 hr. The method for the measurement and the analysis of synthesis rate was the same as that in the previous paper (*2*). There was no decline in the catalytic activity with time.

Results and Discussion

The stationary rate of synthesis obtained is shown in Fig. 1 as a function of total pressure and of flow rate for $N_2 + 3H_2$ system at 305°C. By the same method as in the previous paper (*2*), the data were analyzed and examined for the following three rate equations by using a digital computer (FACOM222).

(a) Temkin equation [Eq. (5) in the previous paper (*2*)];

(b) Langmuir-type equation with main adsorbed species of NH [Eq. (7) in the previous paper (*2*)];

(c) Langmuir-type equation with main adsorbed species of N [Eq. (9) in the previous paper (*2*)]:

$$k = qy_e\left(\frac{1}{P}\right)\left[\frac{-A_2^2y_e^2x}{P} - 0.5\left(1 + \frac{A_2y_e}{P^{1/2}}\right)^2 \ln(1 - x) + 0.5\left(1 - \frac{A_2y_e}{P^{1/2}}\right)^2 \ln(1 + x)\right].$$

The best values of rate constant k, the parameter of equilibrium constant α or A, and the standard deviation S for k are shown in Table 1.

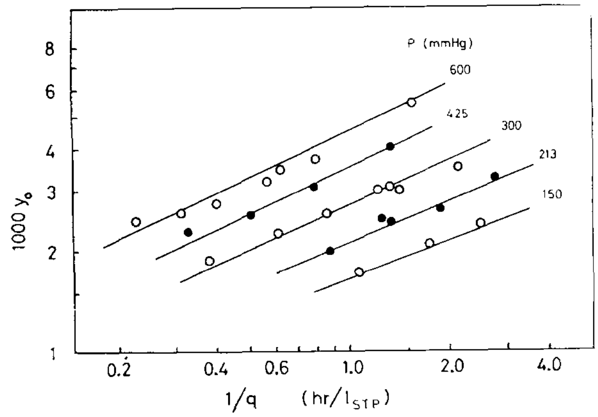

FIG. 1. The stationary rate of ammonia synthesis for $N_2 + 3H_2$ system at 305°C. Each point shows mole fraction (y_0) of ammonia in the gas mixture leaving the catalyst bed against total pressure (P) and flow rate (q); (—) the relationships between y_0 and $1/q$ are calculated for Eq. (c).

TABLE 1
THE BEST CONSTANTS AND STANDARD DEVIATIONS FOR EQS. (a), (b), AND (c)

Eq.	α or A	k	S (%)
(a)	$\alpha = 0.81$	1.06×10^{-2}	35.5
(b)	$A_1 = 5.0 \times 10^2$	2.47×10^{-2}	20.4
(c)	$A_2 = 4.4 \times 10^2$	3.24×10^{-2}	13.4

It is shown that Eq. (c) gives the smallest S value, i.e., the best fit. The relationships between y and $1/q$ are reproduced in Fig. 1 as a solid line for Eq. (c) with the constant given in Table 1.

The synthesis runs with H_2–D_2 mixtures were carried out at 305°C and 425 mm Hg of total pressure. The results are shown in Fig. 2. Equation (c) is applied to these results to obtain A_2 values for different deuterium concentrations taking the k value of 3.24×10^{-2}. The relationships between y and $1/q$ were reproduced with constants thus obtained for the H–D mixtures, and are shown as solid lines in Fig. 2. The relative values of A_2 for mixtures (A_{2M}) are plotted against the deuterium concentration (f_D) of the mixture referring to A_2 of hydrogen system (A_{2H}) in Fig. 3. The relative value (A_{2M}/A_{2H}) should be equal to the relative value of equilibrium constants of the ammonia decomposition (K_{2M}/K_{2H}) on the basis of the assumption made for Eq. (c) (2). The theoretical values of K_{2M}/K_{2H} obtained in the previous paper (2) are

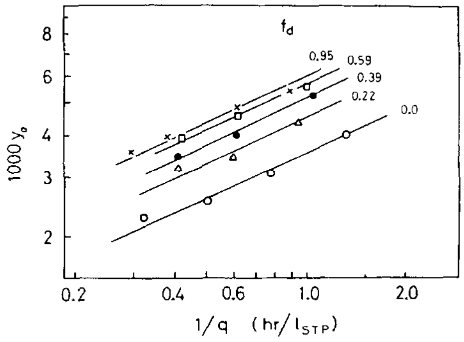

FIG. 2. The stationary rate of ammonia synthesis for $N_2 + 3(H_2$–$D_2)$ system at 305°C and 425 mm Hg of total pressure. Each point shows mole fraction (y_0) of ammonia against flow rate (q) and atomic D fraction (f_D); (—) the relationships between y_0 and $1/q$ calculated for Eq. (c).

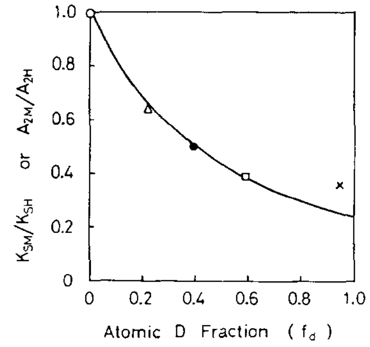

FIG. 3. Isotope effect of A_2 (A_{2M}/A_{2H}) of Eq. (c) against atomic D fraction (f_D); (—) the relative value of the equilibrium constant of ammonia decomposition reaction (K_{SM}/K_{SH}) as a function of f_D.

shown by a solid line in Fig. 3. The agreement between the relative values of A_2 and the calculated line is satisfactory except the point at $f_D = 0.95$.

Thus all the results obtained with the singly-promoted iron are essentially the same as those on unpromoted iron (*2*), that is, the kinetic results are expressed by the Langmuir-type rate equation with the main adsorbed species of N assuming that the reaction rate is determined by the dissociative adsorption of nitrogen, and the inverse deuterium isotope effect is explained by the thermodynamical reason.

Such a similarity in the kinetic behavior seems to be reasonable on the ground of the known effect of the alumina promoter, which has been believed to prevent the sintering of metallic iron in the catalyst without change in the reaction mechanism (*4*). Thus the different adsorbed species found on the doubly-promoted catalyst may be ascribed to the role of potash promoter as has been expressed by us (*2*).

The rate-determining step of ammonia synthesis over the singly-promoted iron has been shown by Tanaka *et al.* (*5*) to lie in the dissociation of nitrogen molecule. Both the present result and the previous result on the unpromoted iron are in conformity with this accepted mechanism.

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