JOURNAL OF CATALYSIS 13, 232–237 (1969)

Kinetics and Isotope Effect of Ammonia Synthesis over an Unpromoted Iron Catalyst

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Received September 16, 1968; revised October 11, 1968

The kinetics and deuterium isotope effect of the ammonia synthesis reaction over unpromoted iron catalyst have been studied at 305°C. Some runs were carried out with mixtures of hydrogen and deuterium. The kinetic data as well as the isotope effect indicate that the rate-determining step is the chemisorption of nitrogen on a surface mainly covered with nitrogen atoms, and not with NH radicals as previously concluded for the doubly promoted catalyst. This result suggests that a part of the role of potash promoter is the change of the adsorbed species which retards the chemisorption process.

INTRODUCTION

The mechanism of ammonia synthesis over an iron catalyst has long been investigated by many workers. Ozaki, Taylor, and Boudart (*1*) have reported an inverse isotope effect found in the synthesis over a doubly promoted catalyst, where deuterium reacted three or four times faster than hydrogen. Such a high inverse effect has seldom been found and must be of a thermodynamic origin. Indeed, the isotope effect has been explained by the difference in the adsorptions of ammonia and deutroammonia to form the imino radical as an adsorbed species which retards the reaction rate. The favored adsorption, i.e., the high retardation of light ammonia, has been evidenced by a statistical calculation.

The above conclusion has not been examined with any singly promoted or unpromoted catalyst. A rate equation over singly promoted catalyst has been given by Kubota and Shindo (*2*) with imino radical as the main species. Very few rate equations have been reported with unpromoted catalyst (*3*), probably because of poor reproducibility of catalytic activity. Thus the kinetics and isotope effect of ammonia synthesis over the unpromoted catalyst have been investigated by a similar method as previously reported (*1*).

EXPERIMENTAL

The iron catalyst used was prepared by precipitation from ferric nitrate (extra-pure grade) with aqueous ammonia solution, followed by washing, pelleting by means of extrusion, drying at 200°C and heating to 525°C. The weight of catalyst used was 10.4 g before reduction. The catalyst was reduced at 400°C by circulating dry hydrogen until no consumption of hydrogen was detected. It took 200 hr. The synthesis gas was prepared by decomposition of ammonia. Deuteroammonia was prepared by the reaction of heavy water and magnesium nitride. The deuterium gas thus obtained was 95% D.

The apparatus used was essentially a closed circulating system and was almost the same as employed in the previous work (*1*). Some modifications were made. That is, the variation of pressure was measured by a cathetometer. The flow meter reading was calibrated by a soap film meter operatable at reduced pressures. The reactor was held in an aluminum block, the temperature of which was maintained within ±0.5°C by an electric controller.

The attainment of a stable activity was not so simple in the present case of the unpromoted iron catalyst and thus much more effort than in the case of the doubly pro-

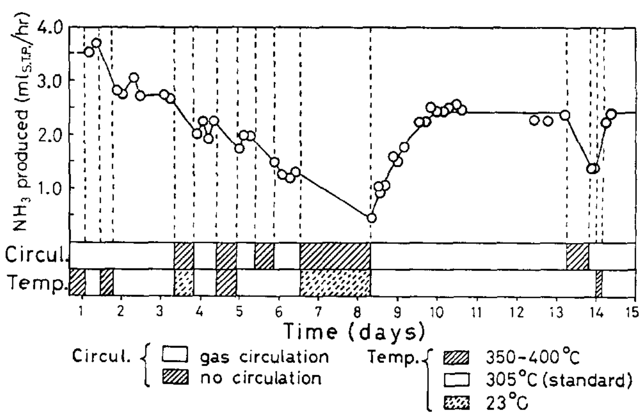

FIG. 1. Activity change with time after various pretreatments. Activity (conversion) was measured under the standard conditions: temperature, 305°C; total pressure, 245 mmHg; flow rate, 1.22 liter STP/hr. Circul. and Temp. in diagram denote the conditions of pretreatments.

moted catalyst was devoted to getting a stable activity. Figure 1 shows the time course of catalyst activation during which various tests were made. It may be seen that, at a fixed flow rate (1.22 l/hr) and temperature (305°C), the catalytic activity was lowered by an interruption of the circulation for some hours or by cooling the reactor to room temperature overnight. Another run without the liquid nitrogen trap also resulted in a drop in the activity. Thus the runs were continued every day and night without interruption. It was found that the activity gradually increased with time until it reached a plateau value after 2 days of the run. A temporary rise in temperature gave a favorable effect on the attainment of a steady rate. After a stable activity was attained, a faster response was obtained to variations in the flow rate or in the pressure.

RESULTS

All the data are represented in graphical form as log-log plots in Figs. 2 and 3. The flow rate of synthesis gas to the catalyst bed is designated by q(l STP/hr). If the measured rate of volume decrease of the reaction system is V(l STP/hr), the mole fraction (y_0) of ammonia in the gas mixture leaving the catalyst bed is given by $y_0 = V/2q$, which is plotted on Figs. 2 and 3. Figure 2 represents the results for deuterium relative to those of hydrogen. It is clear that deuterium reacts faster than hydrogen.

The variation of deuterium concentration in a mixture of hydrogen and deuterium in the course of the reaction with nitrogen was measured at 305°C and 560 mmHg of initial total pressure by trapping ammonia formed. The initial composition was H_2, 30%; D_2, 45%; and N_2, 25%. After 50 hr of runs, 83% of H_2–D_2 gas was consumed, accompanied by a decrease from 60% to 49% in the atomic D concentration of the reactant gas. This small decrease in the D concentration, in spite of the large isotope effect in the reaction rate, must be due to the isotopic equi-

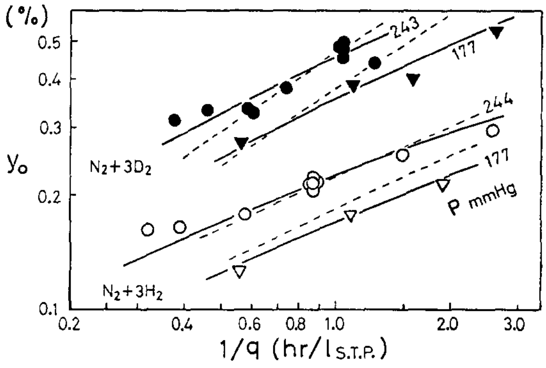

FIG. 2. The results for the deuterium and hydrogen systems at 305°C. Each point shows ammonia concentration (y_0) against total pressure (P) and flow rate (q). The relationships between y_0 and $1/q$ are calculated for Eqs. (7) and (9), and are shown as a dashed line for (7) and a solid line for (9).

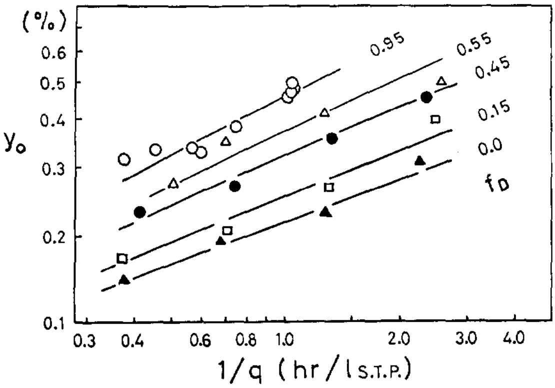

FIG. 3. Some results of H_2–D_2 mixture gas; $N_2 + 3(H_2\text{–}D_2)$. Each point shows ammonia concentration (y_0) against flow rate (q) and atomic D fraction (f_D). The solid lines indicate the relationship between y_0 and $1/q$ calculated for Eq. (9).

libration in hydrogen and ammonia. Anyway, since the decrease in D concentration with time was relatively small, the reaction rate of H_2–D_2 mixture with nitrogen could be measured. The runs with a series of mixtures were made at 305°C and 245 mmHg. Some of these results are shown in Fig. 3.

KINETIC ANALYSIS

The reaction rate R (l NH_3/hr g cat) at any total pressure and ammonia concentration is given from the principle of the flow reactor as follows:

$$R = \frac{1}{W}\frac{dy_0}{d(1/q)} \tag{1}$$

where W is the catalyst weight (g). As Fig. 2 shows a linear relationship

$$n \log y_0 = \log c - \log q \tag{2}$$

may be assumed. Then, the reaction rate R is given by the equation

$$R = \frac{1}{W}\frac{c}{n}y_0^{(1-n)} \tag{3}$$

where n and c are constants. The best value of n which fit the data independent of total pressure was 2.70, and the dependency of c on total pressure was found to be of 2.35 order, although Eq. (3) is just an empirical expression of the reaction rate. The backward reaction must be taken into account for a theoretical treatment of the reaction rate.

The following three equations derived on the assumption of the rate-determining step of nitrogen adsorption were examined.

(a) *Temkin equation*

$$R_1 = \frac{dy_0}{d(1/q)} = k_1 P_{N_2}\left(\frac{P_{H_2}^3}{P_{NH_3}^2}\right)^{\alpha} - k_2\left(\frac{P_{NH_3}^2}{P_{H_2}^3}\right)^{1-\alpha} \tag{4}$$

The integral form of the Temkin equation is

$$k = qP^{1+\alpha}\int_0^x \frac{x^{2\alpha}}{1-x^2}\,dx \tag{5}$$

where $k = k_1^{0.5-\alpha}k_2^{0.5+\alpha}(\frac{1}{4})^{0.5-\alpha}(\frac{3}{4})^{-1.5}$.

(b) *Langmuir-type equation with the main adsorbed species of NH.*

$$R_2 = \frac{dy_0}{d(1/q)} = \frac{k_1P_{N_2} - k_2K_1^2P_{NH_3}^2/P_{H_2}^2}{(1 + K_1P_{NH_3}/P_{H_2})^2} \tag{6}$$

The integral form of Eq. (6) is

$$k = qy_e(1/P)[-A_1^2y_e^2x - 0.5(1 + A_1y_e)^2 \ln(1 - x) + 0.5(1 - A_1y_e)^2 \ln(1 + x)] \tag{7}$$

where $A_1 = 4K_1/3$, $k = k_1/4$.

(c) *Langmuir-type equation with the main adsorbed species of N.*

$$R_3 = \frac{dy_0}{d(1/q)} = \frac{k_1P_{N_2} - k_2K_2^2P_{NH_3}^2/P_{H_2}^3}{(1 + K_2P_{NH_3}/P_{H_2}^{1.5})^2} \tag{8}$$

The integral form of Eq. (8) is

$$k = qy_e\left(\frac{1}{P}\right)\left[\frac{-A_2^2y_e^2x}{P} - 0.5\left(1 + \frac{A_2y_e}{P^{1/2}}\right)^2 \ln(1 - x) + 0.5\left(1 - \frac{A_2y_e}{P^{1/2}}\right)^2 \ln(1 + x)\right] \tag{9}$$

where $A_2 = (\frac{4}{3})^{1.5}K_2$, $k = k_1/4$. The common notations for above three equations are as follows: P(total pressure), $P_{H_2} = 3P/4$, $P_{N_2} = P/4$, $y_0 = P_{NH_3}/P$, $y_e = P_{NH_3,e}/P$, $x = P_{NH_3}/P_{NH_3,e}$; $_e$ denotes the values at equilibrium.

A kinetic equation which incorporates the experimental results shown in Fig. 2 was selected from the above three in the following way using an electronic computer. The values of the k's were calculated for assumed values of α, A_1, or A_2 by substituting observed data for x, P, and q of the integral forms (5), (7), and (9). When N sets of data of x, P, and q are available, an average value

k_{av} is given by $k_{av} = \Sigma^N k/N$ and the standard deviation S is given by $S^2 = \Sigma^N(k\text{-}k_{av})^2/k_{av}^2/(N\text{-}1)$. In this way a number of values α(or A_1, A_2) were tried to get a k_{av} which gave a minimum value of S. The best values thus obtained are shown in Table 1.

TABLE 1

The Best Constants and Standard Deviations for Eqs. (5), (7), and (9)[a]

Eq.	System	α or A	k	S (%)
(5)	H	$\alpha = 0.67$	0.00554	21.1
	D	$\alpha = 0.69$	0.00088	21.6
(7)	H	$A_1 = 840$	0.0282	15.8
	D	$A_1 = 600$	0.0818	18.0
	D*	$A_1 = 164^*$	0.0282	22.4*
(9)	H	$A_2 = 1000$	0.0722	10.4
	D	$A_2 = 370$	0.0952	14.3
	D*	$A_2 = 293^*$	0.0722	14.5*

[a] Asterisks show the values for the deuterium system which have the same k as that for hydrogen system. The ratio of A: $A_{1D}/A_{1H} = 0.205$ for Eq. (7), $A_{2D}/A_{2H} = 0.29$ for Eq. (9).

It is obvious that the least standard deviation was obtained with Eq. (9) irrespective of the isotopic species of hydrogen. Since k was defined as the rate constant of the step of nitrogen chemisorption, the value of k should be the same for hydrogen and deuterium. In this respect also, Eq. (9) is the best one. Equation (5) may be ruled out for this reason. Thus the values of A and S for the deuterium system were calculated with Eqs. (7) and (9) on the assumption that the value of k is the same as that for the hydrogen system and are shown in Table 1 with asterisk. By the use of the modified values of A and k for the deuterium system, the relationships between y and $1/q$ were calculated for Eqs. (7) and (9), and are shown as a dashed line for (7) and a solid line for (9) on Fig. 2. It is clear that Eq. (9) gives a better fit.

Equation (9) was further examined by applying it to the runs with H_2–D_2 mixture, taking the k value of 0.0722 for all the runs. The value of A_2 thus obtained was used together with the above value of k to reproduce the relationship between y and $1/q$ for the mixtures. The reproduced relationship is shown as the solid lines on Fig. 3. The lines fit the experimental points fairly well. The relative values of A_{2m} above obtained for mixtures are plotted against the deuterium concentration (f_D) of the mixture referring to A_2 of hydrogen system in Fig. 4. It is to be noted that the plots regularly deviate from the value expected for the additivity.

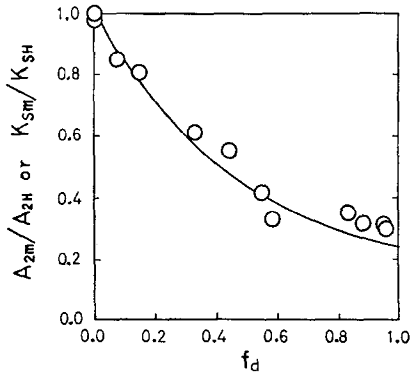

Fig. 4. Isotope effect for A_2 (A_{2m}/A_{2H}), indicated by ○, of Eq. (9) against atomic D fraction (f_D). The solid line indicates the relative value of the equilibrium constant of the ammonia decomposition reaction (K_{sm}/K_{sH}) as a function of f_D.

Discussion

1. Isotope Effect

From the above result it is found that Eq. (9) is the best one to describe the present experimental result, while the previous result on the doubly promoted catalyst was best described by Eq. (7). If Eq. (9) is valid for the result, the relative value of A_{2m} as shown in Fig. 4 must be explained on the basis of the assumption made for Eq. (9).

Since A_2 is proportional to K_2 which appeared in Eq. (8), the relative value of A_2 is identical with that of K_2. According to Eq. (8), K_2 is defined as the equilibrium constant of the dissociative adsorption

$$NH_3 \rightarrow N(a) + 1.5H_2$$

the relative value of K_2 (K_{2m}/K_{2H}) is reduced to the relative value of the equilibrium constant (K_s) of the ammonia decomposition reaction

$$NH_3 = 0.5N_2 + 1.5H_2$$

The value of K_s for hydrogen system (K_{sH}) is known and that for the mixture (K_{sm}) can be calculated as follows:

$$K_{sm} = \frac{[N_2]_e^{0.5}([H_2]_e + [HD]_e + [D_2]_e)^{1.5}}{[NH_3]_e + [NH_2D]_e + [NHD_2]_e + [ND_3]_e}$$

All the equilibrium concentrations of isotopic molecules which appear in this expression were calculated from the value of K_{sH} (16.7 at 305°C) and from the known value of equilibrium constants of the exchange reactions between isotopic molecules (*4*):

$H_2 + D_2 = 2HD \qquad K_1 = 3.71$
$HD + NH_3 = H_2 + NH_2D \qquad K_2 = 2.53$
$D_2 + NHD_2 = HD + ND_3 \qquad K_3 = 1.05$
$NH_3 + NHD_2 = 2NH_2D \qquad K_4 = 3.00$
$ND_3 + NH_2D = 2NHD_2 \qquad K_5 = 2.98$
(305°C)

The relative values of K_s (K_s/K_{sH}) thus obtained are shown by solid line in Fig. 4. The agreement between the relative values of A_2 and the calculated line is satisfactory. This result demonstrates the validity of the assumption made for Eq. (9).*

2. *Reaction Mechanism on the Unpromoted Iron Catalyst*

The inverse isotope effect on the unpromoted iron catalyst found in this study is, as described above, explained by a mechanism similar to the previously reported one (*1*). Namely, the isotope effect on the reaction rate is ascribed to the difference in the equilibrium concentration of adsorbed species that retards the rate of the nitrogen dissociation, the rate-determining step. However there is one change in the mechanism: the main adsorbed species is N(a), while it was NH(a) on the doubly promoted iron.

It has been shown by the study of displacement of adsorbed nitrogen accompanied by isotopic mixing that there are two adsorbed species, undissociated and dissociated nitrogen, on the unpromoted iron, with the former being predominant (*5*). If this conclusion is applied to the synthesis reaction, the reaction scheme may be written as

$$\begin{tikzcd} N_2 \arrow[r, rightleftharpoons, "\text{I}"] \arrow[rr, bend right, "\text{II}'"'] & N_2(a) \arrow[r, "\text{II}"] & N(a) \arrow[r, rightleftharpoons, "\text{III}"] & NH_3 \end{tikzcd}$$

with the step II or II′ being rate-determining. The main adsorbed species of N(a) derived from the kinetic analysis in the present study is the main species that retards the rate-determining dissociation of nitrogen.

It was suggested in the previous paper (*1*) that the main species of NH(a) might be due to a less thorough reduction of the catalyst, because there were some reports (*8*) which supported the main species of N(a) over the doubly promoted catalyst. However those papers, together with a later publication (*6*) which supported N(a), were mainly concerned with the synthesis reaction at a higher temperature, around 450°C, while both the previous and the present work were carried out at around 300°C. Hence the conflicting conclusions on the main species might be caused by the difference in the reaction temperature, i.e., N(a) at high temperature and NH(a) at low temperature. If this is so, the different adsorbed species derived by the two studies on the isotope effect under similar reaction conditions might be due to differences in the catalyst.

The change in the main species from NH to N finds its analogue in the hydrocracking of ethane over iron catalysts. Cimino, Boudart, and Taylor (*7*) have reported that the main species change from $C_2H_2(a)$ on unpromoted iron to $C_2H_4(a)$ on potash-promoted iron. It can be induced from these results that the addition of potash to iron reduces the extent of dissociation of ethane or ammonia on the surface. This would be reasonable because the addition of the electron-donating potash is expected to increase the electron concentration in iron and to result in the reduction of bonding ability of the metal. A part of the promotor action of potash in the ammonia synthesis

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* A similar treatment can be made for Eq (7). However the value of A_{1D}/A_{1H} calculated by Eq. (7), 0.205, was less than one-half of that expected by K_{1D}/K_{1H}, 0.435, where the partition function ratio $Q_{NH(a)}/Q_{ND(a)}$ was estimated in a similar manner to that in the previous report.

may be explained on this basis, while this does not mean that only the addition of potash is effective.

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