

The Effect of Potassium Oxide upon the Decomposition of Ammonia over Iron Synthetic Ammonia Catalysts

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The decomposition of ammonia was carried out in a flow system over three different well-reduced iron synthetic ammonia catalysts (A, with 4.72% alumina, 0.31% potassium oxide and 0.05% silica as promoters; B, with 2.03% alumina, 0.81% potassium oxide and 0.61% silica, and C, with 4.72% alumina, 0.24% potassium oxide and 0.05% silica) at a total pressure of one atmosphere and in the range of 378 to 454°C.

The rate observed was proportional to $(P_{\text{N}_2}/P_{\text{H}_2}^{1.5})^\alpha$ (α : constant) and the activation energy was found to be in the range of 35.0-50.5 kcal/mol over catalysts (A) and (B). On the other hand, on catalyst (C) the rate was proportional to $(P_{\text{N}_2}/P_{\text{H}_2}^{0.5})^\beta$ (β : constant) with the activation energy of 15 kcal/mol.

From these results, it was concluded that the decomposition is controlled by the desorption of adsorbed nitrogen over catalysts (A) and (B), whereas with the decreased amount of potassium oxide the dehydrogenation of adsorbed amino $\text{NH}_2(a)$ controls the decomposition. In connection with these results, the promoter action upon decomposition was briefly discussed.

In addition, it was shown that the kinetics of the decomposition over catalyst (A) was sensitively affected by the reduction conditions of the catalyst.

INTRODUCTION

The effects of potassium oxide and alumina upon ammonia decomposition or the synthetic reaction over iron synthetic ammonia catalysts have been frequently discussed (1-8).

Love and Emmett (5) previously found that decomposition over the singly promoted iron catalyst 954 (containing 10.2% alumina) proceeded with different kinetics than that over the doubly promoted iron catalyst 931 (containing 1.3% alumina and 1.59% potassium oxide). Later, Love and Brunauer (6) prepared various iron synthetic ammonia catalysts by soaking the unreduced singly promoted iron catalyst 191 (containing 0.42% alumina) in potas-

sium hydroxide solutions of different concentrations and studied the decomposition of ammonia. These authors found that the activation energy of the decomposition and the inhibiting effect of hydrogen upon the decomposition increased with increasing amounts of potassium oxide. Similarly, Krabetz and Peters (7, 9) found that potassium oxide exerted an influence upon the activation energy of the synthesis.

On the other hand, Kobayashi *et al.* (10) previously reported that potassium oxide existed as two different forms in the catalyst. One was soluble in water whereas the other was insoluble. The activation energy of the synthesis decreased with increasing amounts of insoluble potassium oxide and finally attained a constant value above 0.5%. Later, it was found (11, 12) with the aid of the optical and electron microscopes that the iron synthetic ammonia catalysts were composed of two different grains: One

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contained 0.58% potassium oxide at most whereas the other contained more.

Emmett *et al.* (13, 14) concluded from adsorption experiments that partially hydrogenated nitrogen such as $\text{NH}(a)$ or $\text{NH}_2(a)$ existed predominantly on the singly promoted catalyst whereas on the doubly promoted catalyst these species did not exist in appreciable amount.

In view of the facts described above, the present work was attempted to study the role of potassium oxide in ammonia decomposition over iron synthetic ammonia catalysts.

APPARATUS AND PROCEDURE

Three different iron synthetic ammonia catalysts were used: Catalyst (A) with 4.72% alumina, 0.31% potassium oxide and 0.05% silica as promoters; catalyst (B) with 2.03% alumina, 0.81% potassium oxide and 0.61% silica and catalyst (C), containing 4.72% alumina, 0.24% potassium oxide and 0.05% silica. Catalyst (C) was prepared by immersing the unreduced catalyst (A) in distilled water for 72 hr, and potassium oxide in the catalyst was partly dissolved in water as potassium hydroxide. The amount of potassium oxide in catalyst (C) was estimated from the difference between the amount originally present and that dissolved in water.

The catalyst was carefully reduced in a stream of hydrogen at a flow rate of 500 cc (STP)/min. The weight of the catalyst (before reduction) and its reduction schedule are summarized in Table 1.

After the catalyst had been reduced, the decomposition was carried out at a total pressure of 1 atm in a flow system and the effect of gaseous components upon the rate of the decomposition* was determined in the same manner as described previously (15).

The rate was determined from the difference between the inflow rate and the outflow of ammonia since the % decomposi-

* The rate was practically independent of the partial pressure of nitrogen as already reported (15).

TABLE I
THE REDUCTION SCHEDULE AND THE WEIGHT OF THE CATALYSTS

Series No.	Temperature (°C)	Time (hr)
Catalyst A used: 10 g (Apparent Volume: 3.5 cc)		
I ^a	450	45
II ^a	550	94
III ^a	600	94
Catalyst B used: 7.1 g (Apparent Volume: 2.5 cc)		
XVI	450	48
XVII	600	24
Catalyst C used: 10 g (Apparent Volume: 3.5 cc)		
XI	450	45
XII	600	60

^a Cited from the previous paper (15).

tion was small.** Gases used were carefully purified in the same manner as in the previous work (15).

The surface area and the composition of promoters on the catalyst surface were determined by the conventional methods of Brunauer, Emmett and Teller (16) and Emmett and Brunauer (17), respectively, for each of the batches of catalysts used in the decomposition experiments.

RESULTS

Table 2 shows the surface area and surface compositions of promoters on the various catalysts reduced at different temperatures. It is seen that decomposition on catalyst (A) did not change appreciably with the rise of the reduction temperature. The results on catalyst (B) were somewhat different. As the reduction temperature was raised, the proportion of iron on the surface of the catalyst increased and that of po-

** The rate was determined within an error of about $\pm 5\%$. Exceptionally, in the series I experiment about 80% of the ammonia was decomposed at the most. Since the rate observed in this series was of almost zeroth order in the partial pressures of hydrogen and ammonia, it could still be approximated by the difference between the inflow and the outflow rate of ammonia. In other series experiments, the percent of the decomposition was nearly 10%. Therefore, such approximation could be valid in the present experiments.

TABLE 2
 THE SURFACE AREA AND THE SURFACE COMPOSITIONS OF PROMOTERS

Reduction		V_m^a	V_{CO}^b	$V_{CO_2}^b$	Fe %	K ₂ O %	Al ₂ O ₃ %
Temp. °C	Time hr						
Catalyst A							
450	37	4.18 (18.1) ^c	0.79	1.10	19.2	26.7	55.1
550	88	3.37 (14.8) ^c	0.62	0.96	18.4	28.5	53.1
600	67	2.74 (12.0) ^c	0.495	0.80	18.0	29.2	52.8
Catalyst B							
450	45	2.96 (12.9) ^c	0.80	1.19	27.3	31.1	41.6
600	40	2.49 (10.9) ^c	0.92	1.10	36.5	23.2	40.3
Catalyst C							
450	45	4.16 (18.2) ^c	0.95	0.74	22.8	17.8	59.4
600	60	3.52 (15.2) ^c	0.72	0.79	20.6	22.6	56.8

^a V_m : Volume of nitrogen monolayer adsorption per gram by BET method at -195°C .

^b V_{CO} or V_{CO_2} : Volume of carbon monoxide or carbon dioxide adsorbed per gram of catalyst.

^c Figures in the brackets show the surface area per gram of catalysts m^2/gr .

tassium oxide decreased. That of alumina remained practically constant, however. The proportions on catalyst (C) did not change appreciably. The proportion of potassium oxide was smaller compared to those obtained on the other two catalysts.

The rate r (cc/min g catalyst) of decomposition was expressed in the present experiments as

$$r = kP_{\text{NH}_3}^x/P_{\text{H}_2}^y, \quad (\text{i})$$

where k , x and y are constants. P_{NH_3} and P_{H_2} represent the partial pressures of ammonia and hydrogen, respectively.

In Table 3, x and y values, and the ratio y/x are listed with the values of the activation energies of the decomposition.

Both x and y increased markedly from the Series I to II experiments. These differences in x and y were attributed to the reduction of the catalyst at 550°C after Series I. In the determination of the ratio y/x for Series I, a large error was introduced due to the change in composition of gas in passing through the catalyst. Therefore, the effect of reduction upon the ratio is ambiguous. Once catalyst (A) was reduced at 550°C , the ratio as well as x and y were practically unchanged by further reduction at 600°C (See Series II and III experiments). The values obtained on catalyst

(B) were independent of the reduction temperature. On catalyst (C), x increased by further reduction but the ratio y/x was unchanged.

The activation energies of the decomposition are listed in the last column of Table 3. The value obtained on catalyst (C) was much smaller than those obtained on catalysts (A) and (B).

DISCUSSION

The results thus far obtained on doubly promoted iron catalysts were interpreted in terms of the Temkin-Pyzhev rate equation (18). It was, therefore, concluded that the rate-determining step is the desorption of adsorbed nitrogen which is the only adsorbed species. Substantial evidence in support of this mechanism was that the ratio was 1.5. This could hold either on nonuniform or uniform surface (19).

As is evident from Table 3, the ratios y/x obtained in series II and III on catalyst (A), and in series XVII on catalyst (B) are close to 1.5. The activation energies were obtained to be in the range of 35.0–50.5 kcal/mole.

Accordingly, it was concluded that the desorption of adsorbed nitrogen is rate-determining for the decomposition in these series of experiments. Our results fairly ac-

TABLE 3
THE EXPERIMENTAL VALUES OF EXPONENTS x and y ,^a AND THE ACTIVATION ENERGY OF THE DECOMPOSITION

Series No.	Temp. (°C)	x	y	y/x	Activation Energy kcal/mol
Catalyst A					
I ^b	423	0.17 ± 0.05 (0.078)	0.07 ± 0.03 (0.099)	0.41 ± 0.21 (1.27)	43.5 (44.2)
II ^b	424	0.40 ± 0.08	0.63 ± 0.03	1.58 ± 0.30	31.0 (38.5)
III ^b	424	0.41 ± 0.05	—	—	48.0 (50.5)
	432	—	0.65	1.58 ^c	
Catalyst B					
XVI	417	0.55 ± 0.03	—	—	45.0 (48.0)
XVII	426	0.47 ± 0.05	0.65	1.38	34.0 (35.0)
Catalyst C					
XI	378	0.43 ± 0.06	0.18 ± 0.02	0.42 ± 0.08	14.9 (15.0)
XII	426	0.60 ± 0.13	0.24 ± 0.04	0.40 ± 0.10	—

^a x and y represent the reaction orders of the rate equation $r = kP_{\text{NH}_3}^x/P_{\text{H}_2}^y$. The values in the brackets were estimated after the correction had been made for the change in the partial pressure of component gases along the catalyst bed.

^b Cited from the previous paper (15).

^c Estimated from x - and y -values obtained at 424 and 432°C, respectively.

corded well with those obtained by other workers (1-5, 20, 21) over the doubly promoted iron catalyst, nonpromoted iron and the evaporated iron film.

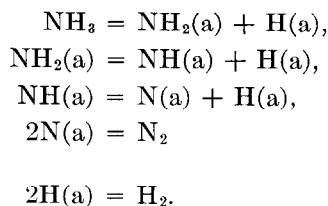
In contrast, the results on catalyst (C) gave the ratios of 0.42 and 0.40 at 378 and 426°C, respectively. The activation energy was found to be 15 kcal/mole, almost one third those obtained on catalysts (A) and (B). In case the pore diffusion of the reactants was rate-determining or nitrides were formed during the decomposition, its value might be lowered (1, 19). It was revealed, however, from the work by Wheeler (22), Lehrner (23) and Emmett, *et al.* (24) that both those effects could be negligible.*

Ozaki, Boudart and Taylor (25) recently concluded that the ammonia syn-

thesis is inhibited strongly by the presence of adsorbed imino NH(a) on a poorly reduced doubly promoted iron catalyst although nitrogen adsorption is rate-determining. If the decomposition proceeds by this mechanism, the desorption of adsorbed nitrogen is rate-determining but it is inhibited by the presence of adsorbed imino. Therefore, the rate can be approximately expressed (19) as

$$r = k(P_{\text{NH}_3}/P_{\text{H}_2})^a/P_{\text{H}_2} \quad (\text{ii})$$

for either the nonuniform or uniform catalyst where the decomposition was assumed to proceed through the scheme



* It was estimated from Wheeler's theory (22) that 95% of the surface of catalyst (C) participated in the decomposition.

and

The k and a are constants. Hence, the ratio $y/x = (1 + a/a)$. Since x is nearly zero in the Series I experiment, y should be close to one. Equation (ii) is, therefore, invalid for the results in Series I. Similarly, the results in the other series do not conform to (i).

Takezawa and Toyoshima (15, 19, 26) recently studied the ammonia decomposition over catalyst (A) and found that the ratio y/x was near 0.5 at temperatures above 479°C with an activation energy of 22 kcal/mol. From these results, it was concluded that the dehydrogenation of adsorbed amino $\text{NH}_2(a)$ is rate-determining at high temperatures. In this respect, the present results obtained on catalyst (C) could be interpreted in terms of this mechanism.

From the adsorption experiments (13, 14), partially hydrogenated nitrogen could be present on the singly promoted iron catalyst in appreciable amounts, whereas nitrogen is predominantly present on the doubly promoted iron catalysts. Such a marked difference in the adsorbed species on these catalysts was also found in the recent study of the effect of hydrogen upon the nitrogen equilibration reaction (27) i.e., the reaction was markedly influenced by the presence of hydrogen on the singly promoted iron catalyst, whereas on the doubly promoted catalyst the hydrogen produced no effect. In this respect, it is possible that during the synthesis or decomposition, hydrogenated nitrogen predominates with decreasing potassium oxide. Therefore, partially hydrogenated nitrogen could be present appreciably during the decomposition on catalyst (C). However, it is still a problem why potassium oxide affects the rate.

As was evident from the results in the Series I experiment, the reaction orders were sensitively affected by reduction of the catalyst. However, the effect could not be interpreted.

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