

KINETICS AND MECHANISM OF AMMONIA DECOMPOSITION OVER ALUMINA SUPPORTED NICKEL CATALYSTS

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Decomposition of Ammonia over two alumina supported nickel catalysts containing 10 and 15 per cent nickel, has been studied in the temperature range 400°–600°C. The results indicate that the rate of decomposition increases with increasing partial pressure of ammonia (P_{NH_3}) and decreases with increase of hydrogen partial pressure (P_{H_2}) whereas nitrogen appears to have no significant effect.

In the temperature range 400°–440°C the rate approximately follows the expression

$$-dP_{\text{NH}_3}/dt = k (P_{\text{NH}_3}/P_{\text{H}_2})^{0.45}$$

At about 460°C the order of the reaction with respect to ammonia changes from 0.45 to 1.0 and so in the temperature range 460°–500°C the rate conforms to

$$-dP_{\text{NH}_3}/dt = k (P_{\text{NH}_3}/P_{\text{H}_2})^{0.45}$$

Above 500°C the order of the reaction with respect to hydrogen decreases with increase of reaction temperature and finally at 600°C the rate becomes almost independent of P_{H_2} . So, at 600°C and above the rate equation assumes the form

$$-dP_{\text{NH}_3}/dt = k P_{\text{NH}_3}$$

Probable mechanism of ammonia decomposition over supported nickel catalyst has been discussed based on experimental results and observations.

INTRODUCTION

The catalytic decomposition of ammonia on metal catalysts has been extensively studied by many workers since early part of this century. Study of the process particularly on iron catalysts in flow system was started as early as 1930 in connection with the understanding of mechanism and kinetics of synthesis and decomposition of ammonia. Based on several investigations it was generally accepted that the catalytic decomposition of ammonia proceeded through the successive dehydrogenation of the adsorbed ammonia.

Starting from the generally accepted mechanism that desorption of nitrogen is the rate determining step (cf. Winter 1931; Emmett & Brunauer 1937; and Brunauer & Emmett 1940) and assuming that nitrogen atoms are more prevalent at the catalyst surface than any other adsorbed species containing nitrogen and the rate of adsorption and desorption of nitrogen depends on surface coverage, Temkin and Pyzhev (1939) deduced a rate expression which for ammonia decomposition

can be expressed as

$$-\frac{dP_{\text{NH}_3}}{dt} = k \left\{ \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3} \right\}^{1-\alpha} \quad \dots (1)$$

where P_{NH_3} , P_{H_2} are the respective partial pressures, k is the rate constant and α is another constant which is always less than one and accounts for the heterogeneous character of the catalyst surface. Although kinetic expression derived by Temkin and Pyzhev (1939) could explain to a great extent most of the kinetic data available at that time, several discrepancies were observed by different workers (e.g., cf. Love & Emmett 1941; Emmett & Kummer 1943; and Brill 1951).

Following those discrepancies several investigators have suggested alternatives to the Temkin-Pyzhev theory. From the determination of the stoichiometric number, Enomoto *et al.* (cf. Enomoto & Horiuti 1952; and Enomoto *et al.* 1955) concluded that one of the steps of dehydrogenation of ammonia on catalyst surface is rate determining. Horiuti and Toyoshima (1957, 1958) have shown that the dehydrogenation of surface imide radical is the rate determining step.

Ozaki *et al.* (1960) proposed a mechanism which assumes that the desorption of nitrogen is rate limiting but the surface is covered with imide radicals.

Takezawa and Toyoshima (1966) inferred from their investigation on the decomposition of ammonia over doubly promoted iron catalyst that the rate determining step changes with rise of reaction temperature from the desorption of nitrogen adatoms to one of the steps of dehydrogenation of ammonia on catalyst surface.

The catalytic decomposition of ammonia has been investigated by a number of workers on nonferrous catalysts also. It is generally accepted that the ammonia decomposition on tungsten catalysts is a zero order reaction and its rate is independent of the pressures of hydrogen and nitrogen (cf. Laidler 1954; and Trapnell 1955). The zero order kinetics have been interpreted to indicate the catalyst surface to be fully covered by ammonia (Laidler 1954). Tamaru (1961) found that at lower temperatures ammonia decomposed to produce only hydrogen, all the nitrogen being taken up by tungsten and the initial rate of this reaction was independent of ammonia pressure. This was explained by the rapid saturation of the catalyst surface with surface imide followed by nitride formation.

The kinetics of the decomposition of ammonia on copper Hastelloy C and Inconel surfaces has been investigated by Nozik and Behnken (1965). Their results generally support the Ozaki-Taylor-Boudart mechanism (Ozaki *et al.* 1960) for ammonia decomposition.

The decomposition of ammonia on molybdenum has been studied by Tsuchiya and Ozaki (1969). The initial rate of ammonia decomposition was observed to be independent of ammonia pressure above a certain level similar to the findings of Tamaru on tungsten.

The present work had as its primary objective the elucidation of the kinetics and mechanism of ammonia decomposition over alumina supported nickel catalyst and thereby derive a rate equation for it.

EXPERIMENTAL SECTION

Experiments were carried out in a flow system employing a small stainless steel reactor, which is shown schematically in Fig. 1. Hydrogen, ammonia, argon or nitrogen from commercially available cylinders after purification were used as feed. Each feed gas flow was individually measured accurately by capillary flowmeter. The purifications of the feed gases consist of drying ammonia over fused potassium

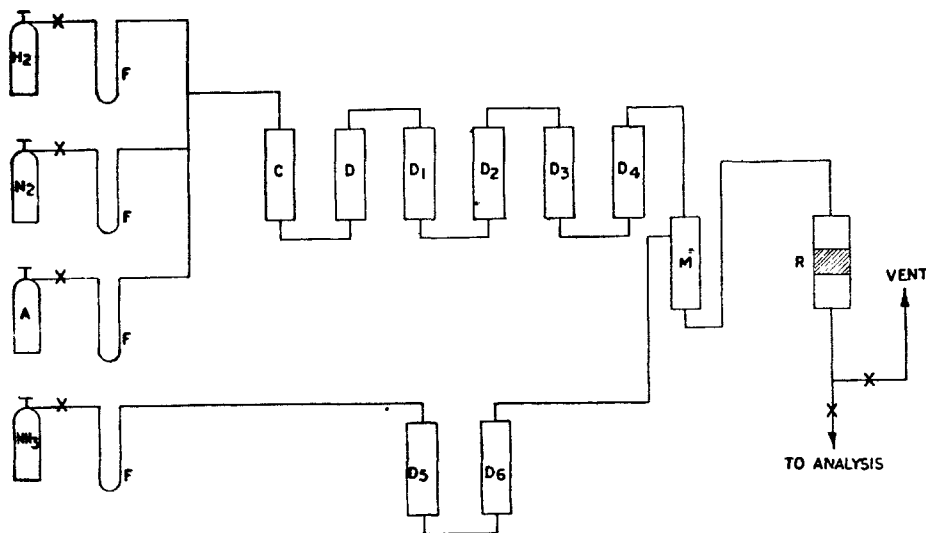


FIG. 1. Schematic diagram of Ammonia Decomposition Unit. F, Flow Meter ; C, Tube filled with Cu-wire ; D, De-Oxotube ; D_1, D_2 , etc. Drying Towers ; D_1, D_2 , Silica gel ; D_3, D_4 , Magnesium perchlorate ; D_5, D_6 , Potassium Hydroxide ; M, Mixer ; R, Reactor.

hydroxide and passing the mixture of H_2 and A or N_2 through a tube containing copper wire maintained at $300^\circ C$ to $340^\circ C$, then through deoxo-tube and finally through a series of towers packed with silica gel and magnesium perchlorate.

2 ml. of catalyst particles of 10 to 14 mesh size was supported on a stainless steel gauge at the middle of the reactor the internal diameter of which is 2.2 cm. The temperature of the catalyst bed was rigidly controlled by an automatic temperature controller and the incoming and outgoing gas temperatures were measured by two thermocouples placed at the top and bottom of the catalyst bed.

To determine the dependence of decomposition rate upon the partial pressure of ammonia in the gas mixture, experiments were performed in which partial pressure of hydrogen (P_{H_2}) was held constant and ammonia partial pressure (P_{NH_3}) was varied. Argon was used as diluent to maintain the total inflow (V_T) rate constant at 800 ml./mt. In a like manner the dependence of the rate upon P_{H_2} was obtained.

The undecomposed ammonia in the gas leaving the reactor, was absorbed in standard sulphuric acid solution and the excess acid titrated with a standard sodium hydroxide solution. The rate of decomposition of ammonia was estimated from the difference between the amounts of ammonia entering and leaving the reactor in a given time.

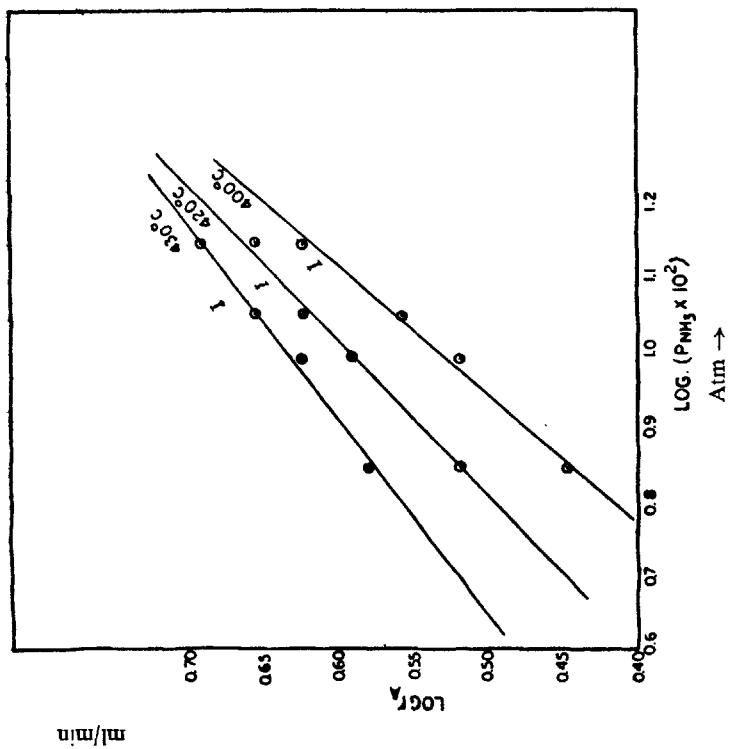


FIG. 2. Effect of partial pressure of ammonia on the rate of ammonia decomposition with catalyst I within the temperature range 400–430°C.

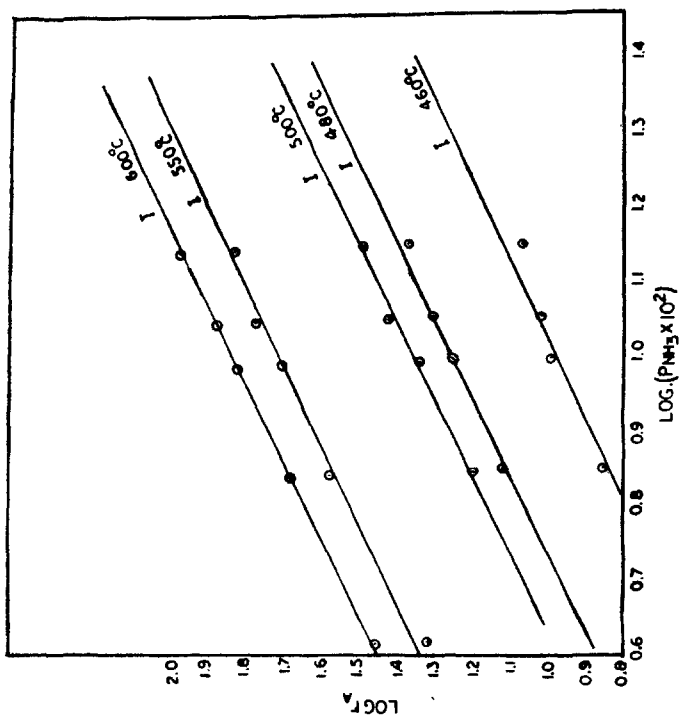


FIG. 3. Effect of partial pressure of ammonia on the rate of ammonia decomposition with catalyst I within the temperature range 460–600°C.

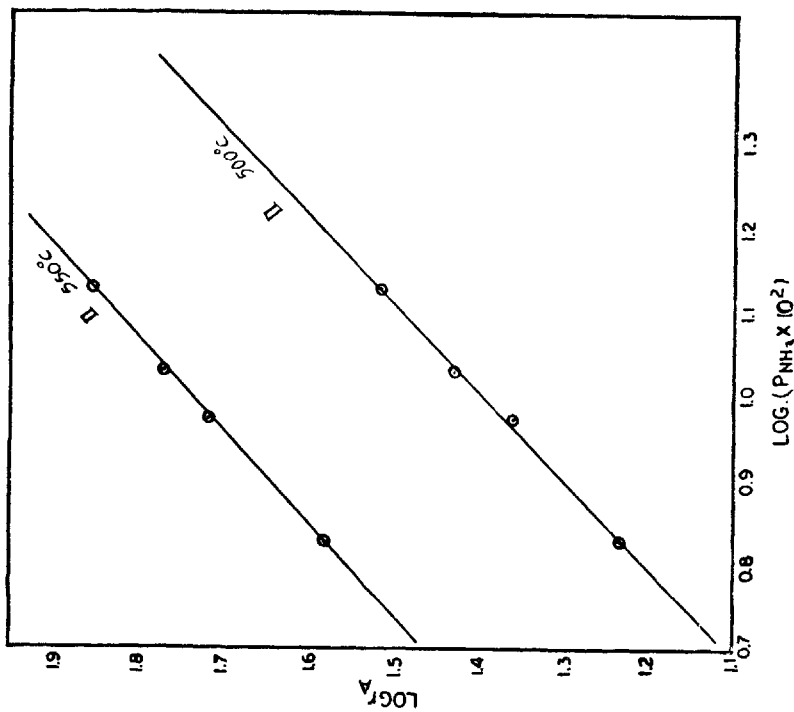


FIG. 5. Effect of partial pressure of ammonia on the rate of ammonia decomposition with catalyst II within the temperature range 500–550°C.

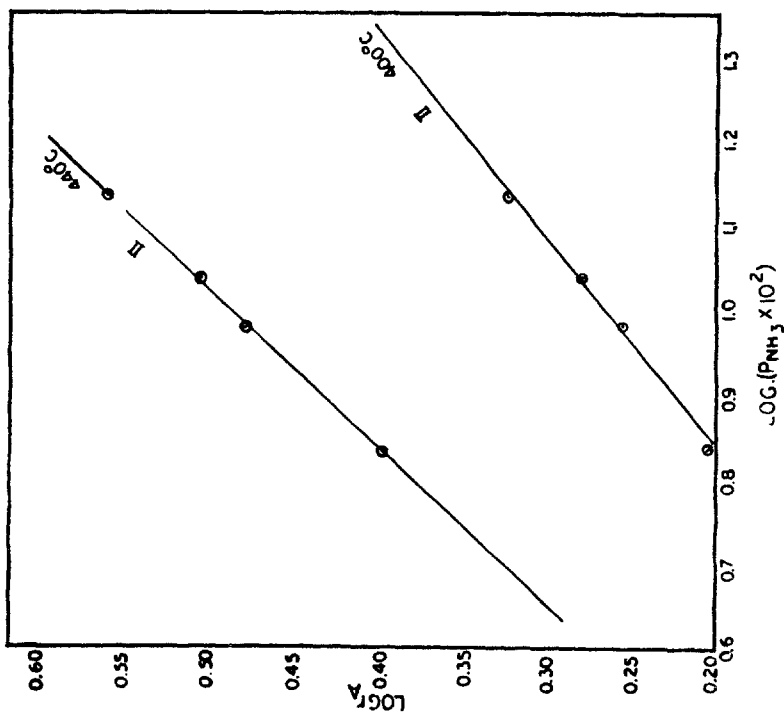


FIG. 4. Effect of partial pressure of ammonia on the rate of ammonia decomposition with catalyst II within the temperature range 400–440°C.

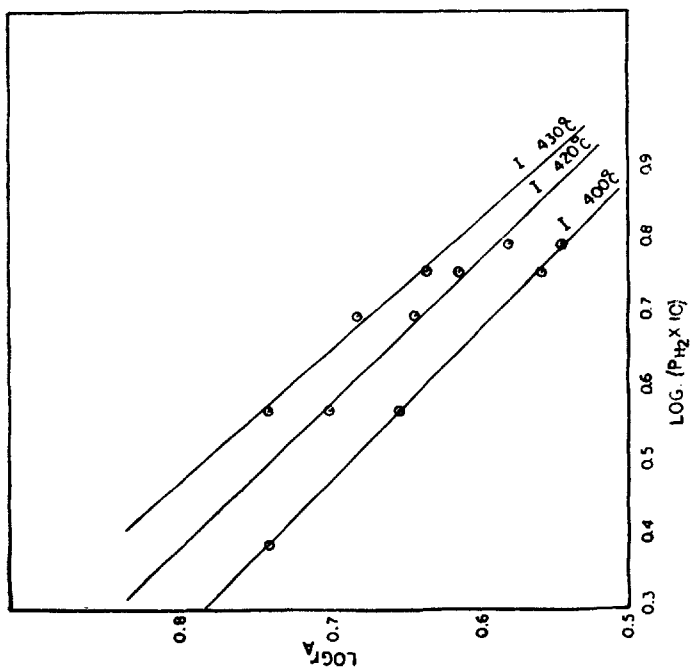


Fig. 6. Effect of partial pressure of hydrogen on the rate of ammonia decomposition with catalyst I within the temperature range 400–430°C.

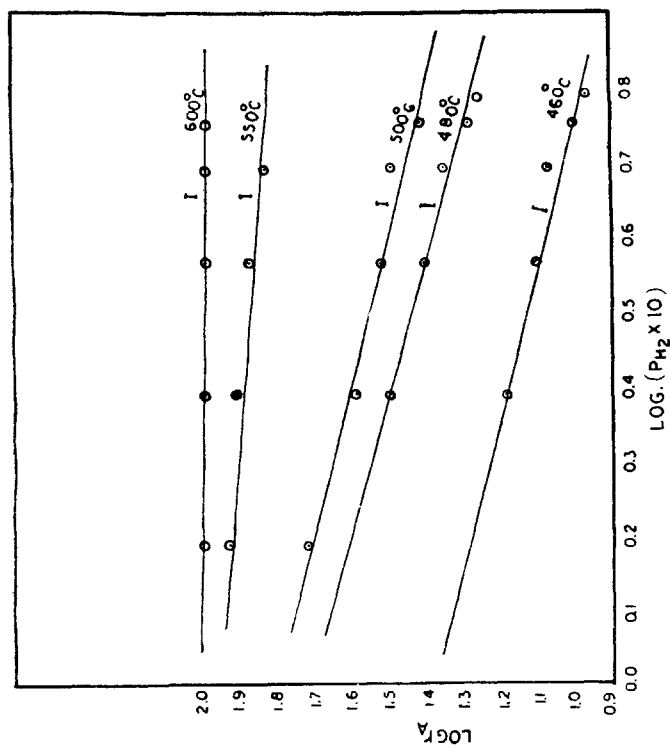


Fig. 7. Effect of partial pressure of hydrogen on the rate of ammonia decomposition with catalyst I within the temperature range 460–600°C.

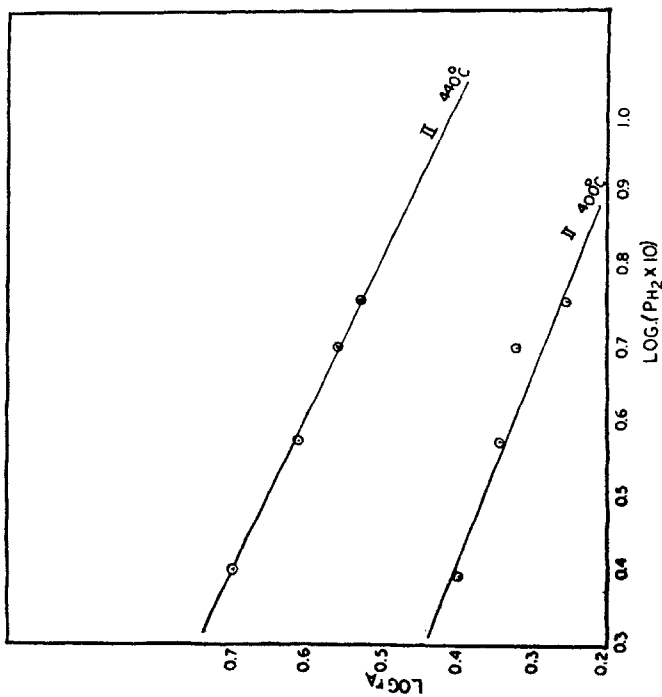


FIG. 8. Effect of partial pressure of hydrogen on the rate of ammonia decomposition with catalyst II within the temperature range 400-440°C.

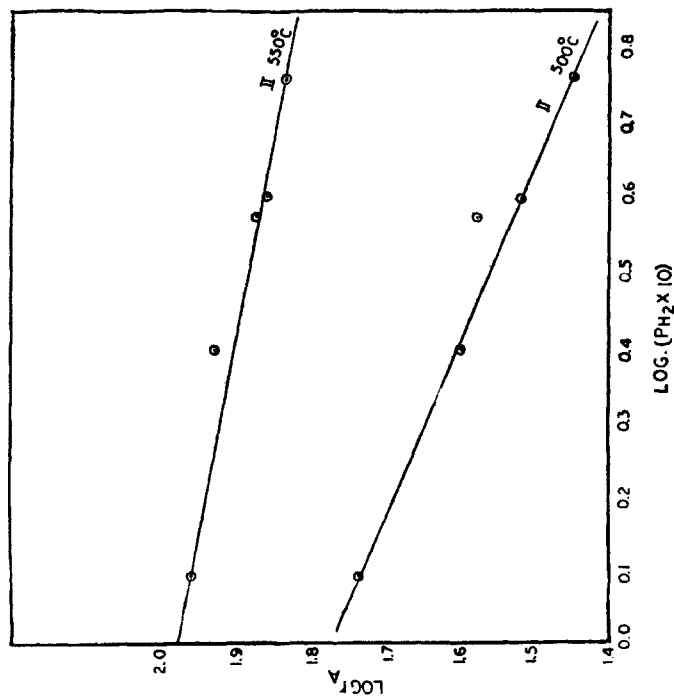


FIG. 9. Effect of partial pressure of hydrogen on the rate of ammonia decomposition with catalyst II within the temperature range 500-550°C.

Two series of experiments were carried out in the temperature range of 400°C to 600°C corresponding to two alumina supported nickel catalysts containing 10 and 15 per cent nickel designated as catalyst I & II respectively. The catalyst in each case was reduced at 500°C in a stream of argon and hydrogen mixture for a period of 24 hours to ensure complete reduction.

Prior to actual experiments a series of blank tests were carried out, maintaining reactor temperature in the range of 400°C to 600°C but without using any catalyst to see the wall effect of the reactor on the decomposition rate. The extent of decomposition in all such blank tests were negligible.

RESULTS

Figures 2 to 9 show the variation of rate of ammonia decomposition (r_A) with P_{NH_3} and P_{H_2} at different temperatures of the experiments. The slopes of the straight lines give order m and n of the reaction with respect to ammonia and hydrogen respectively. Table I shows the values of m and n thus obtained at different temperatures.

TABLE I
Experimental values of m and n at different temperatures

Temperature °C	m	$-n$	$-n/m$
<i>Catalyst I</i>			
400	0.54	0.50	0.93
420	0.42	0.50	1.20
430	0.40	0.45	1.10
460	0.93	0.50	0.52
480	1.00	0.55	0.55
500	1.00	0.44	0.44
550	1.00	0.20	0.20
600	0.97	0.044	0.05
<i>Catalyst II</i>			
400	0.41	0.43	1.05
440	0.50	0.46	0.92
500	1.00	0.44	0.44
550	1.00	0.21	0.20

The effect of nitrogen on the decomposition rate has been shown in Table II. The last column of the table shows the ratio of the decomposition rate in the presence of argon (r_A) and the same in the presence of nitrogen (r_N). This ratio, r_A/r_N is very nearly equal to one at all temperatures of the experiments showing that there is no significant effect of nitrogen on the decomposition rate in presence of the catalysts used in the present investigation.

DISCUSSION

The rate equation for the catalytic decomposition of ammonia can be generally expressed as

$$-\frac{dP_{\text{NH}_3}}{dt} = k P_{\text{NH}_3}^m P_{\text{H}_2}^{-n} \quad \dots \quad (2)$$

TABLE II
Effect of Nitrogen on the rate of decomposition

Temp. °C	P_{NH_3} atm	P_{H_2} atm.	P_{A} atm	P_{N_2} atm.	Ammonia decomposed ml. at NTP/min.	$r_{\text{A}}/r_{\text{N}}$
<i>Catalyst I</i>						
400	0.139	0.492	0.369	0	4.2	1.10
400	0.139	0.492	0	0.369	3.8	
420	0.139	0.492	0.369	0	4.5	1.08
420	0.139	0.492	0	0.369	4.4	
500	0.139	0.492	0.369	0	30.3	1.03
500	0.139	0.492	0	0.369	29.5	
500	0.070	0.492	0.438	0	24.7	0.97
500	0.070	0.492	0	0.438	25.5	
600	0.137	0.493	0.370	0	92.5	0.99
600	0.137	0.493	0	0.370	93.3	
600	0.069	0.247	0.684	0	48.6	1.01
600	0.069	0.247	0	0.684	48.2	
<i>Catalyst II</i>						
400	0.136	0.494	0.370	0	2.1	1.05
400	0.136	0.494	0	0.370	2.0	
400	0.135	0.499	0.366	0	3.6	1.06
400	0.135	0.499	0	0.366	3.4	
550	0.058	0.540	0.402	0	36.5	0.99
550	0.058	0.540	0	0.402	36.8	

where k is the rate constant at a given temperature and m and n are also constants. Results of the present investigation indicate that the rate of ammonia decomposition over the temperature range of experiments increases with increasing partial pressure of ammonia and decreases with hydrogen partial pressure. Nitrogen appears to have no significant effect on the rate of decomposition. Table I shows that the values of m and n change significantly within the temperature range of the experiments. In other words the order of the reaction with respect to both ammonia and hydrogen change considerably as the temperature is increased within the range of 400°C to 600°C.

Thus, in the temperature range of 400°C to 440°C, the values of both m and n are more or less constant around 0.45 within the limits of experimental error, so that the ratio n/m is nearly equal to 1 and the rate expression assumes the form,

$$-\frac{dP_{\text{NH}_3}}{dt} = k \frac{P_{\text{NH}_3}^{0.45}}{P_{\text{H}_2}^{0.45}} \quad \dots \quad (3)$$

These results do not support Temkin-Pyzhev theory according to which the value of n/m should be 3/2. On the other hand, the kinetic data within the temperature

range of 400°C to 440°C appear to closely follow the Ozaki-Taylor-Boudart mechanism which predicts the value of n/m as 1. The kinetic data for ammonia decomposition over non-ferrous surfaces obtained by Nozik and Behnken (1965) were also found to support the Ozaki-Taylor-Boudart mechanism and they obtained values for m and n both nearly equal to 0.5 which is close to our results.

On increasing the temperature from 440°C to 460°C, the order of the reaction with respect to ammonia increases from 0.45 to 1 while that with respect to hydrogen remains practically constant at about 0.45. So, the rate expression at 460°C can be written as,

$$\frac{dP_{\text{NH}_3}}{dt} = k \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{0.45}} \quad \dots \quad (4)$$

This shows that between 440°C and 460°C there is a region where the order of the reaction with respect to ammonia changes from 0.45 to 1. Mardaleishvili *et al.* (1967) observed a similar region above 450°C where the order of ammonia decomposition over Pd, Ni, Mo and Quartz, with respect to ammonia changed from 0.5 to 1. Takezawa and Toyoshima (1966) also reported a change in the order of ammonia decomposition reaction over promoted iron catalyst on increasing the temperature from 425°C to 479°C. But they observed, the change in the order of reaction with respect to both ammonia and hydrogen. However, the value of n/m obtained by Takezawa Toyoshima (1966) at 479°C was 0.5 as against 0.45 obtained in the present investigation at 500°C. Since they observed an inhibitive effect of nitrogen at higher temperature it was argued that the rate determining step changed from desorption of nitrogen at lower temperature to one of the dehydrogenation steps of ammonia at higher temperatures. No such shifting of rate determining step with increase of temperature can be explained with our results since no inhibitive effect of nitrogen is observed at any temperature as shown in Table II.

On further increase of temperature beyond 500°C, the order of the reaction with respect to ammonia remains constant at 1 but that with respect to hydrogen continuously decreases and becomes very low at 600°C. Thus, at 600°C where the influence of hydrogen partial pressure is insignificant the rate expression tends to assume the following form

$$\frac{dP_{\text{NH}_3}}{dt} = k P_{\text{NH}_3} \quad \dots \quad (5)$$

Mardaleishvili *et al.* (*loc cit.*) also indicated a similar rate expression at higher temperature using Pd, Ni, Mo and quartz as catalysts.

From the foregoing observations it appears reasonable to believe that ammonia decomposition over supported nickel catalyst follows the Ozaki-Taylor-Boudart mechanism. However, with increase of temperature, formation of surface nitride from surface imide takes place as the adsorption of hydrogen decreases. Ultimately, at temperature above 600°C where virtually no hydrogen is adsorbed, the surface is completely covered with adsorbed nitrogen and the rate of desorption of nitrogen depends on surface nitride concentration which in turn depends on ammonia concentration, the other intermediate steps being very fast. This can clearly explain the

enhanced influence of ammonia and decreasing influence of hydrogen on the rate at higher temperatures.

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