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The Catalytic Decomposition of Ammonia

Electric Field Effect on the Catalytic Activity

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The decomposition of ammonia over a Pt-Rh-Pd catalyst has been studied in an electric field. At a given temperature, the activity and resistance of the catalyst are significantly increased by the field. A negative potential on the catalyst causes a decrease in the temperature of the catalyst accompanied by a corresponding increase in the temperature near the anode. The increase in temperature is probably caused by recombination reactions of ions in the gas phase. The effect of the field is greatest the first 15-25 hr of the catalyst lifetime, decreasing continuously with time. A corresponding decrease in the ion current was observed but the decrease in ion current was about ten times faster than the decrease in catalytic activity. In this study, ions were observed in a system of H_2 and in a H_2-N_2 mixture. However, for these systems, the electric field did not change the temperature of the catalyst and of the gas flow. These results indicate that the catalyst participates as an energy carrier to the gas volume, thus initiating reactions there. A two-stage mechanism is proposed for the catalytic decomposition of ammonia.

INTRODUCTION

The catalytic decomposition of ammonia produces charged particles in the zone around the catalyst (*1*) and proceeds through a hetero-homogeneous mechanism, as shown by previous papers (*2-4*). Experiments designed to detect the polarity of the charged particles showed that negative and in some cases positively charged particles were present (*1*). The measured current density of the negatively charged particles was up to 10^{-3} amp cm^{-2} and that of the positively charged particles up to 10^{-7} amp cm^{-2}.

In 1962 Melton (*5*) detected mass-spectroscopically the formation of NH_4^+ by the catalytic decomposition of ammonia on a Pt catalyst heated above 500°C. In the same year, Fogel and collaborators (*6, 7*), investigating the same reaction by means of secondary ion-ion emission, found a number of ionic species such as H^-, Pt^-, PtN^-, PtN_2^-, NH_2^-, H^+, N^+, Pt^+, NH_2^+, H_2^+, NH^+, and NH_3^+. Melton and Emmett (*8*) confirmed the presence of three free radicals N, NH, and NH_2 and of the ions NH_2^- and NH_4^+ in the gas phase around the catalyst.

The investigations (*9*) about the nature of the active nitrogen carried out so far have shown that it decomposes the ammonia to nitrogen and hydrogen. The vibrationally excited nitrogen molecules in their ground electronic state have proved active towards the ammonia molecules. The same results were found for the radicals NH which possess a chemical activity sufficient to cause the splitting of a hydrogen atom from the chemically stable molecules without any activation energy.

EXPERIMENTAL

The experiments were carried out with a flow system. The apparatus consisted of a Supermax tube of 20-mm ID and 40 cm long (Fig. 1). The catalyst—a Pt-Rh-Pd wire—was drawn from a gauze for catalytic oxidation of ammonia. The wire was 0.08 mm in diameter, its length varying with the experiments (15 to 25 mm), U-curved, and placed

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* D. Vladov died on July 25, 1965.

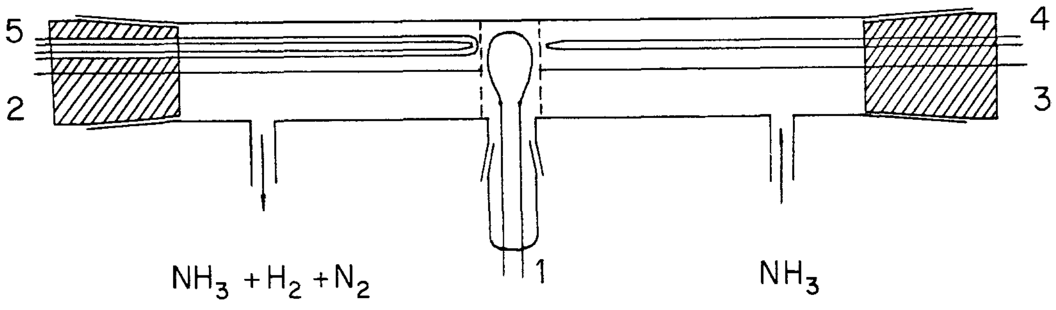

FIG. 1. Scheme of the apparatus: 1, catalyst; 2 and 3, Pt electrodes; 4 and 5, thermocouples Pt — Pt, Rh.

perpendicular to the flow direction. Two planar Pt electrodes (18-mm diameter) were placed at a distance of 2 to 5 mm in front and behind the catalyst. All experiments were carried out at a pressure of about 700 mm Hg.

The temperature in the volume of the reaction space was measured by means of two thermocouples situated immediately behind the two electrodes. One of them was put in a protective glass tube.

The experiments were carried out with ammonia grade A (containing less than 0.2% water), nitrogen-hydrogen mixture 1:3 (resulting from the catalytic decomposition of NH_3), and oxygen-free hydrogen. The nitrogen-hydrogen mixture and hydrogen were dried on Blaugel.

A constant flow rate through the reaction vessel was maintained by a rheometer. The catalyst was heated between 700° and 1300°C (DC from an accumulator cell) as measured by an optical micropyrometer (±5°C). The catalyst heating current and its potential were measured with instruments class 0.5. Subsequently the catalyst was connected shoulder-wise to a Wheatstone bridge, thus making possible the continual measurement of its resistance.

A potential difference of up to 600 V was created between the catalyst and one of the electrodes and the volt-ampere characteristics were read. The current was measured by means of a galvanometer (maximum sensitivity of 1.1×10^{-9} amp/scale division). Most of the experiments were carried out when the catalyst was polarized negative.

The quantity of the decomposed ammonia was determined by means of a laboratory gas interferometer (±0.03 vol %).

RESULTS

A series of volt-ampere characteristics read at different temperatures for the same catalyst is shown in Fig. 2. The catalyst temperature was lowered 20° to 100°C by the application of a potential difference (catalyst negative) between the catalyst and

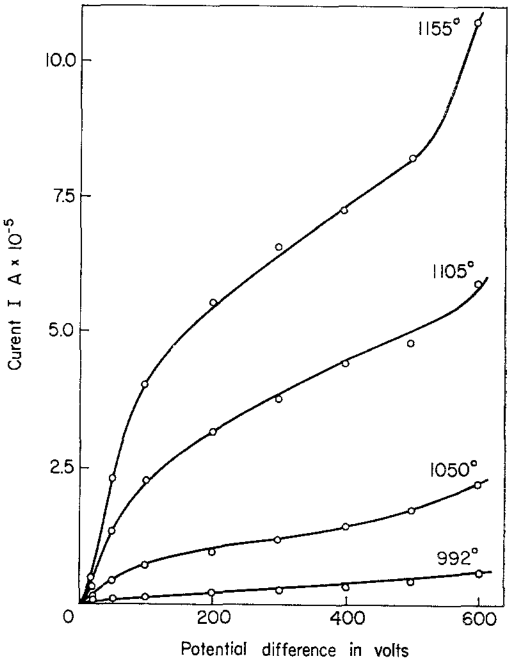

FIG. 2. Volt-ampere characteristics of a NH_3 flow. Linear rate of the flow: 3.35 cm sec^{-1}; catalyst surface, 0.050 cm^2.

one of the net electrodes when the catalyst temperature was greater than 900°C and a potential difference of greater than 100 V was applied. A constant catalyst temperature was maintained for the data of Fig. 2 by increasing the catalyst heating current to compensate for the decrease in temperature caused by increasing potential. The increase in power (ΔW) required to maintain a constant temperature is shown in Fig. 3.

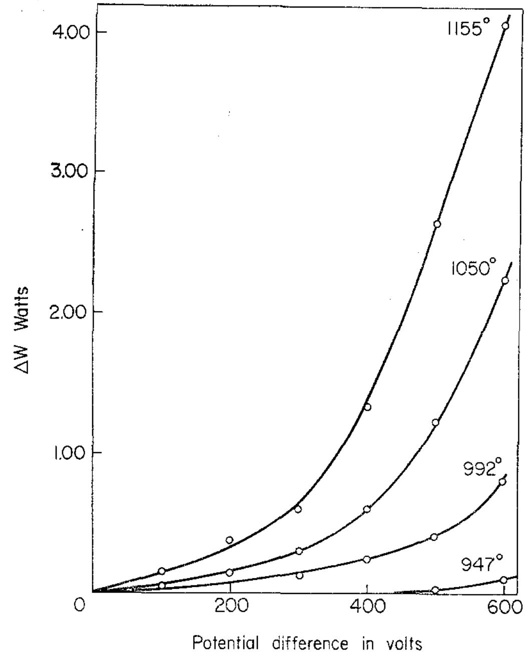

Fig. 3. Increase of power (ΔW) of catalyst heating current. Power of the heating current at a potential difference 0 V.

Temp. (°C):	1155°	1050°	992°	947°
Power (W):	10.72	8.36	7.03	5.78

The rate of decomposition of NH_3 is increased by the application of a potential to the catalyst as shown in Fig. 4. The field causes no permanent changes in the catalyst as evidenced by the immediate return to the original state by removal of the field.

During the catalyst action, the influence of the applied potential difference on the catalyst temperature and activity decreases continuously. This influence disappears after 15 to 25 hr, depending on the catalyst temperature. The effects mentioned above may be made appreciable anew when either the potential difference or the catalyst temperature are increased sharply. The ion current from the catalyst also decreased with time but about 10 times more rapidly than the activity of the catalyst. The sharpest decrease was observed in the first 10 working hours of the catalyst. It was found that under a constant field action the intensity of the ion current decreases according to

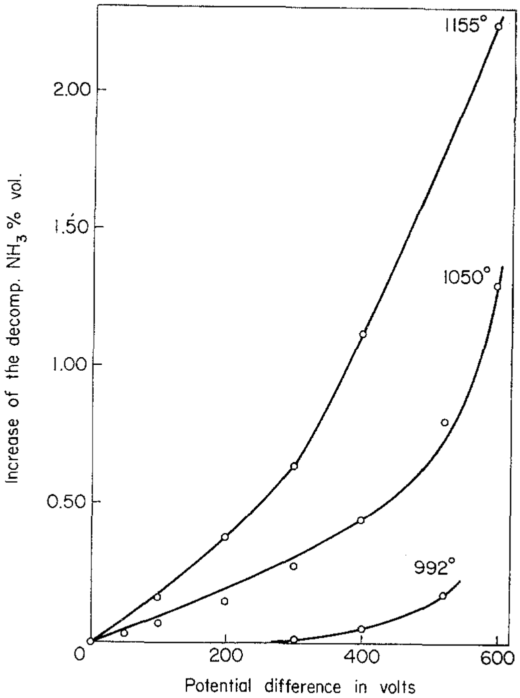

Fig. 4. Increase of quantity of the decomposed NH_3; decomposed NH_3 at a potential difference 0 V.

Temp. (°C):	1155°	1050°	992°
Decomp. NH_3:	9.05	6.63	4.92

$$I = A\tau^{-n}$$

where I is the measured current at constant potential difference, A and n being constants, and τ, the time interval (from the start of the catalyst action). A change in the field caused an immediate change in the rate of current decrease (Fig. 5).

The experiments carried out in a nitrogen-hydrogen flow showed the presence of negatively charged particles, while in a flow of pure air such particles were not detected. In

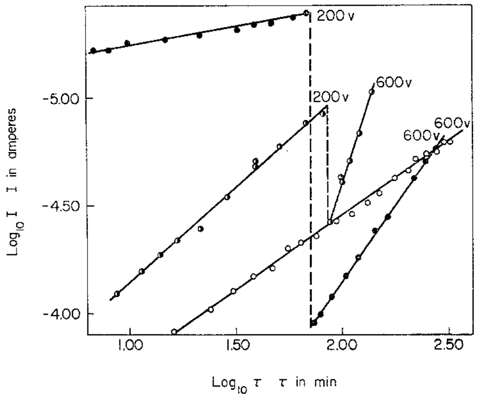

FIG. 5. Catalyst temperature 1155°C; ○, NH_3 flow, 600 V, $\log I = \bar{4}.92 - 0.68 \log \tau$; ●, NH_3 flow, 200 V, $\log I = \bar{6}.94 - 0.16 \log \tau$; 600 V, $\log I = \bar{2}.54 - 1.34 \log \tau$; ◐, H_2-N_2 mixture, 200 V, $\log I = \bar{4}.63 - 0.80 \log \tau$; 600 V, $\log I = 0.88 - 2.74 \log \tau$.

the H_2-N_2 system, the ion current decreased gradually with time similar to that for the NH_3 system (Fig. 5). The volt-ampere characteristics in a H_2-N_2 and in a H_2 flow are similar to those for NH_3 shown in Fig. 2. But, the application of a potential difference as great as 600 V does not change the catalyst temperature appreciably, although the current is close or equal in order to the current measured in an ammonia flow.

Perceptible ammonia decomposition (0.1 vol %) occurs at 750°C, whereas negatively charged particles in a NH_3, H_2-N_2, and H_2 flow are not observed below 830°C.

In the NH_3 system, the resistance of the catalyst at constant temperature depended upon the polarity of the catalyst. A 600-V potential difference (catalyst negative) increased the resistance by about the same amount as an increase in temperature of 30° to 40°C. These differences in the catalyst resistance may be found during the first 10 hr of the catalyst action. Similar results were found for a Pt catalyst.

In the decomposition of NH_3 over tungsten, a measurable current of negatively charged particles was detected above 1050°C. The electric field effect on the catalyst temperature was observed at temperatures of about 1300°C; the ion current was up to 10^{-4} amp cm^{-2} for about 15 vol % NH_3 decomposition.

DISCUSSION

Papers published recently (*10*) proved that the catalytic process taking place on a metal surface may excite strong exo-electronic emission from the catalyst surface. The relations given above, however, do not permit one to identify the described phenomena with an exo-electronic emission. It is most probable that the observed emission due to electrically charged particles results from the interaction between the catalyst and the substrate. The observed decrease in the ion current, following the law of damping of the exo-electronic emission and the decrease in the total activity of the catalyst is due perhaps to structural changes in the catalyst surface layer under the action of the processes ensuing there. The stated influence of the electric field intensity on the rate of the ion current decrease shows that these changes are closely related to the formation and emission of electrically charged particles.

The composition and behavior of the separate current carriers in an ammonia and in a nitrogen-hydrogen flow are different. This conclusion is based on the fact that the electric field has no effect on the temperature and resistance of the catalyst in a hydrogen and nitrogen-hydrogen system.

Considerable amounts of energy are carried away from the catalyst (negative polarity) in the NH_3 system by the action of the electric field as evidenced by the marked influence on temperature, activity, and resistance. The experimental data do not permit one to explain these phenomena. It may be assumed that the creation of an electric field results in an oriented adsorption of the ammonia molecules or it facilitates the desorption of the final products (hydrogen and nitrogen), thus accelerating the reaction rate. However, a similar assumption is contrary to the fact that when the catalyst is polarized as anode (instead of being cathode) the effects are not reversed: A suppression of the decomposition and increase in catalyst temperature could not be observed.

Thus assuming that the creation of an electric field between the catalyst and one of the electrodes does not alter the conditions for heat transfer and heat radiation, it may be expected that the additionally supplied energy (for the maintainance of a constant temperature of the catalyst) will be spent exclusively for the decomposition of new quantities of ammonia.

We denote with Q' the supplied energy with the electric current (heating the catalyst to a given temperature in an ammonia flow) and with Q'_R, the amount of energy necessary to obtain the measured quantity of the H_2-N_2 mixture under the action of the electric field, presuming that the H_2-N_2 mixture is produced by the reaction

$$NH_3 = 1/2N_2 + 3/2H_2 - 13 \text{ kcal} \qquad (1)$$

(The thermal effect is an average value for the temperature interval 900–1300°C). Further we denote with Q'' and Q''_R the same quantities in the absence of electric field. Hence

$$(Q' - Q'_R) = (Q'' - Q''_R)$$

the equation being valid when the catalyst is heated to the same temperature in both cases, i.e., the heat losses from heat transfer and heat radiation being equal.

The experiments carried out showed that in all cases, when the electric field has influenced the catalyst temperature and activity, the following relation is valid:

$$(Q' - Q'_R) - (Q'' - Q''_R) = \Delta Q > 0$$

The calculated difference ΔQ represents the excess energy necessary because of the influence of the field. The differences in thermal conductivity of the flows were taken into account for the calculation of ΔQ. These differences were up to 20% of ΔQ because of the different content of H_2 and N_2. Figure 6 shows $(Q - Q_R)$ as a function of catalyst temperature with and without an electric field. Figure 7 presents the dependence of ΔQ on the catalyst temperature by experiments with three different catalysts. The NH_3 decomposed by the action of the electric field required $\Delta Q = 131 \pm 21$ kcal/mole. The high value of ΔQ shows that charged particles desorbed from the catalyst are removing some of the energy when the field is present.

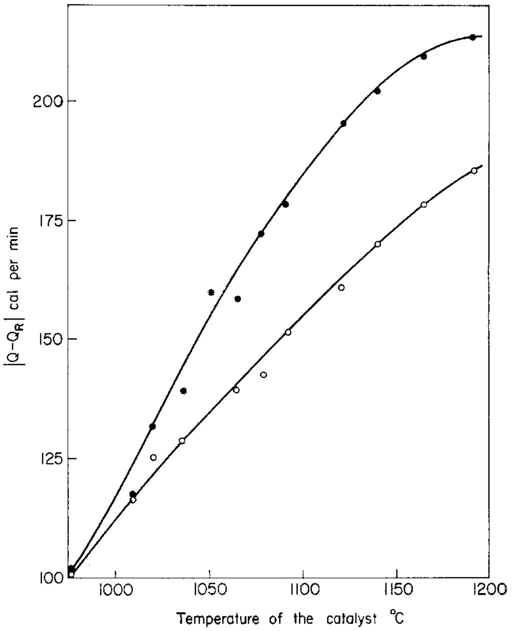

Fig. 6. The dependence of $(Q - Q_R)$ on the catalyst temperature. Linear rate of the flow, 1.33 cm sec^{-1}; catalyst surface, 0.045 cm^2; ●, 600 V; ○, 0 V.

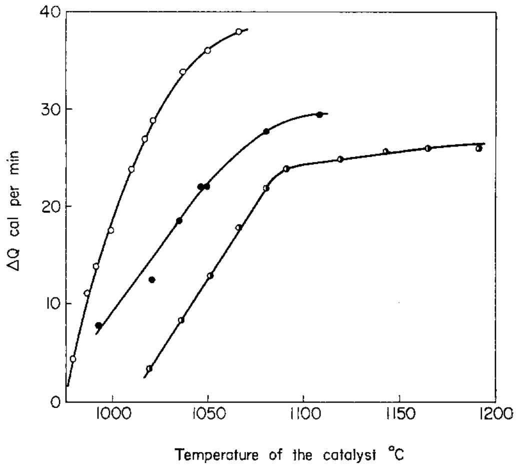

Fig. 7. The dependence of Q (600 V – 0 V) on the catalyst temperature.

To investigate this postulate experimentally, the temperature in the vicinity of the anode was measured. It turned out that for a negative catalyst the temperature near the anode was increased by tens of degrees, independent of the direction of flow. On the opposite side of the catalyst a simultaneous decrease of the same order is observed. Results from two consecutive experiments shown in Fig. 8 give the temperature difference as a function of potential difference. In the first experiment, the front electrode was polarized as anode and in the second, the back electrode. The observed temperature changes could not be explained on the basis of surface recombination because similar results were obtained with a protected thermocouple.

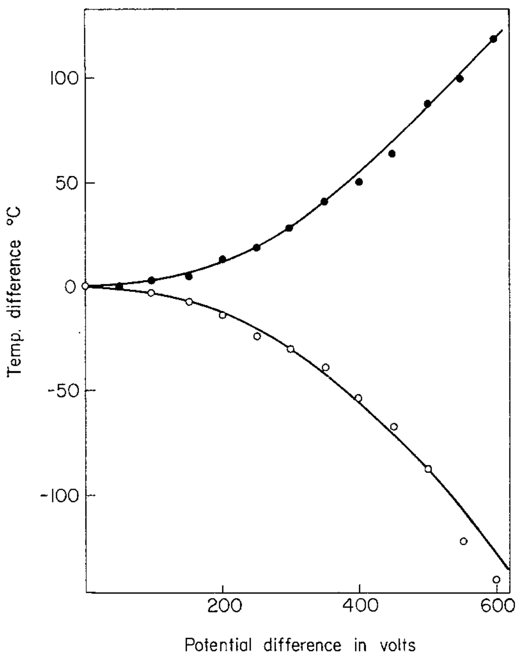

FIG. 8. Temperature change, measured with a Pt-Pt, Rh thermocouple. Catalyst temperature, 1050°C; linear flow rate, 3.36 cm. sec^{-1}; catalyst surface, 0.040 cm^2; ●, front electrode polarized as anode; ○, back electrode polarized as anode.

Temperature changes were not observed in a H_2-N_2 system although the ion current was about the same order as for the NH_3. It seems probable that the changes in temperature are due to recombination of charged particles in the space around the electrodes.

The temperature changes mentioned above could be explained assuming that under the action of the electric field the concentration of the electrically charged active particles in the different zones of the reaction space volume is altered. Consequently, in some zones the exothermal, and in others the endothermal processes, prevail:

A two-stage decomposition of NH_3 on a Pt-Rh-Pd catalyst is proposed on the basis of the experimental data known so far.

First stage: a dissociative adsorption of ammonia related to the decomposition on the catalyst surface

$$NH_3 = NH + H_2 - 89\text{ kcal} \tag{2}$$
$$NH_3 = NH + 2H - 195\text{ kcal} \tag{3}$$
$$NH_3 = NH_2 + H - 104\text{ kcal} \tag{4}$$
$$NH_3 = N + 3H - 227\text{ kcal} \tag{5}$$

A part of the intermediate products (produced on the catalyst surface) is desorbed and the rest of them interact between themselves giving hydrogen and nitrogen.

Second stage: the intermediate products desorbed from the catalyst surface, NH_2, NH, H, and N, interact between themselves and with the ammonia molecules in the gas phase following one of the reaction schemes

$$NH_2 + NH_2 = N_2 + 2H_2 + 85\text{ kcal} \tag{6}$$
$$NH + NH = N_2 + H_2 + 158\text{ kcal} \tag{7}$$
$$NH + NH_2 = N_2 + H_2 + H + 70\text{ kcal} \tag{8}$$
$$NH_2 + H = NH + H_2 + 15\text{ kcal} \tag{9}$$
$$NH + H = H_2 + N + 18\text{ kcal} \tag{10}$$
$$NH + N = N_2 + H + 140\text{ kcal} \tag{11}$$
$$NH_2 + N = N_2 + 2H + 51\text{ kcal} \tag{12}$$
$$\begin{aligned} N_2^* + NH_3 &= N_2 + NH_3^* \\ NH_3^* &= NH_2 + H \end{aligned} \tag{13}$$
$$NH_3 + NH = NH_2 + NH_2 - 16\text{ kcal} \tag{14}$$
$$NH_3 + H = NH_2 + H_2 - 0.2\text{ kcal} \tag{15}$$

where N_2^* and NH_3^* are electronically excited molecules.

In the initial period of catalyst work some of the reactions listed above proceed as ion–molecule or ion–radical reactions. This may elucidate the influence of the electric field on the reaction rate.

The mechanism proposed is in good agreement with the idea (*2–4*) that in the volume around the catalyst, processes take place with a total positive thermal effect.

A question may be raised here: Does the electric field change the mechanism of the reaction for the ammonia decomposition or does it intensify one of the two reaction stages? It was shown that in the course of the catalyst action the influence of the electric field on the temperature and the activity of the catalyst decreases continuously, accompanied with a gradual and weak decrease in its total activity. Having in mind that the decrease in the ion current is related to the occurring structural changes of the catalyst it may be assumed that for the formation of the electrically charged particles more favorable conditions exist in the initial periods of the catalyst action. These particles are produced by a process following one of the reactions (2)–(5). The creation of an electric field during this period of catalyst action facilitates the desorption in the volume of the reaction space, and decelerates the rate of their recombination on the catalyst. The final result is a decrease of the catalyst temperature.

In conclusion, it may be added that the creation of an electric field most probably also has an influence on the percentage of conversion in the ammonia synthesis.

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