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THE THERMAL DECOMPOSITION OF AMMONIA ON IRON CATALYSTS. II

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The development of the following method of investigating catalysts and the results herein reported are the outgrowth of studies on the thermionic properties of the materials and mixtures used as catalysts in the synthesis of ammonia.[1] In order to determine the relative importance of the physical properties of the catalysts and to compare these properties with their catalytic properties, it was necessary to have some measure of the chemical activity of the surface at the same temperature and under as nearly the same surface conditions as when the thermionic measurements were made. The decomposition of ammonia was chosen rather than the synthesis as no appreciable or easily measured amount of ammonia is synthesized at one atmosphere pressure or lower and the present system and methods would not permit of working at higher pressures. The decomposition tests proved satisfactory in every way. The same developments which gave a very uniformly coated catalyst strip as a positive ion source, gave an equally uniform and constant temperature chemically active surface. The temperature of the surface was easily determined within a few degrees and kept constant at the given temperature throughout an entire test. The kinetics of the reaction of such a system are relatively simple in comparison to conditions in a catalyst bed as used in synthesis.

Since the publication of a preliminary account of this work[2] many more tests have been made on these catalyst mixtures, a detailed account of which will follow.

Apparatus.—The main scheme of the arrangement of the apparatus is similar to that used in the previous work[3] and is shown in Fig. 1. Instead of drawn filaments of tungsten, molybdenum or nickel, catalyst-coated platinum strips furnished the hot surface upon which the reaction took place. Very even and uniformly coated surfaces can easily be obtained when the catalyst mixture is first reduced, then finely ground and finally coated onto the strip. In this case the 300-mesh or finer catalyst, which has been ground under benzene, is mixed with paraffin and coated on to the hot strip by means of a glass rod at a temperature just high enough to melt the paraffin. When a thin but uniform layer is obtained on the twisted platinum strip, the temperature is raised by increasing the current through the strip. At a dull red temperature a bright red spot develops at some place on the strip and passes over the entire filament length.

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[1] Kunsman, *Phys. Rev.*, **25**, 892 (1925); *Science*, **62**, 269 (1925); *J. Phys. Chem.*, **30**, 525 (1926); *Phys. Rev.*, **27**, 249 (1926); *Proc. Nat. Acad.*, **12**, 659 (1926); *J. Franklin Inst.*, **203**, 635 (1927).

[2] Kunsman, *Science*, **65**, 527 (1927).

[3] Kunsman, THIS JOURNAL, **50**, 2100 (1928).

This bright spot is due to the heat produced by the rapid oxidation of the finely divided iron granules, and attains a temperature sufficiently high to sinter or fuse the coating to the twisted platinum strip. A coating of any desired thickness can be had by repeating the process as often as desired. This type of coating, even after reduction in hydrogen or nitrogen–hydrogen mixture, is very firmly attached and uniform in temperature. The only disadvantage is that the surface coated with the reduced material is relatively inactive in comparison to surfaces prepared by coating the platinum strip with the unreduced material. In the latter case the coating of the unreduced mixture and paraffin are applied to the filament and raised to a temperature just below visible and allowed to bake for about a half hour, after which another coating is applied and this continued until the desired thickness is obtained. This surface must be handled carefully as portions may break off and destroy the uniformity of the surface. The surface on reduction is very much more active catalytically than the previous one, as will be shown. As the ammonia catalyst is the reduced mixture and not the oxide, care was taken to see that the coated materials were thoroughly reduced either in a nitrogen–hydrogen mixture or hydrogen before the decomposition tests were made.

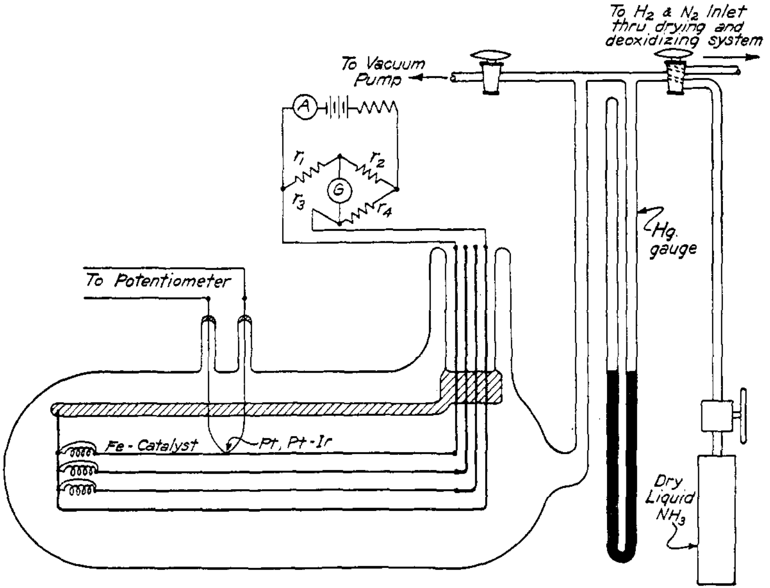

Fig. 1.—Apparatus for the study of the decomposition of ammonia on catalyst coated strips.

The temperature of the coated surface was determined in two ways: first, by means of an optical pyrometer, correcting for the emissivity of the surface and the absorption of the glass, and, second, by means of a thermocouple welded to the platinum strip. In this case the 0.005-cm. diameter Pt–Pt–Ir wire forming the juncture was close to the surface of the catalyst coating. The thermocouple is the more convenient method of determining the temperature and can be used through a wider range of temperatures than the optical pyrometer. Some difficulty was at first encountered in getting these fine wires through a pyrex glass. Any very slow leaks which may result at times at these seals can be closed with de Khotinsky wax.

The temperature as read from the calibrated thermocouple gave an added check on the Wheatstone bridge method of keeping the resistance of the filament and temperature of the hot surface constant throughout the run or until almost the whole of the ammonia was decomposed.

The coated strips were attached at one end through heavy tungsten leads and the other through a molybdenum spring and platinum strip. The function of the spring was to keep the filament taut and of the platinum strip to carry most of the current, so that no parts of the assembly would become appreciably hot except the coated surface. From four to eight amperes was used to heat the coated strip. The decomposition chamber was immersed in running tap water throughout all tests. A mercury trap, not shown in the sketch, separated the decomposition chamber and McLeod gage from the rest of the apparatus after the proper ammonia pressure, usually one-third of an atmosphere, was obtained.

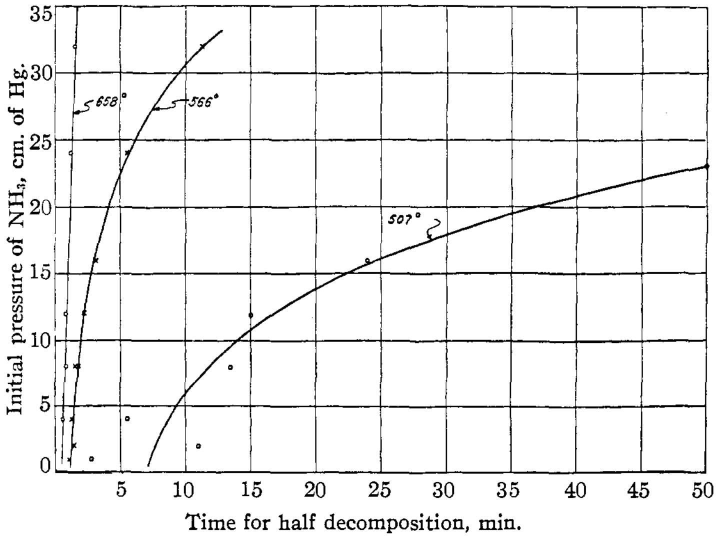

Fig. 2.—The decomposition of ammonia on a Fe–Al–K catalyst at 507, 566 and 658°.

Order of Reaction.—As the results from all the catalyst-coated strips were similar, a detailed account of one catalyst only will be given. In general the system is not as simple as the tungsten or molybdenum. The results obtained in an attempt to determine the order of the reaction are given in Fig. 2. One notices that there was no simple relation between the "half time" and the ammonia pressure, that is, the "half time" had neither a linear variation with the ammonia pressure (test for apparent zero order reaction) nor was it independent of the initial ammonia pressure (test for apparent first order reaction). One cause of this variation is quite evident when we consider the effects of the products of the reaction, nitrogen and hydrogen, on the reaction velocity. This effect can best be shown by referring to Fig. 3. Nitrogen has very little or no effect, while a very marked effect of hydrogen in slowing up of the reaction is apparent at 630°. The data of Fig. 3 were taken four months after those of Fig. 4. The two surfaces, therefore, are not comparable. In the previous results reported for tungsten and molybdenum a small but definite retarding effect was observed for hydrogen and but very little or no effect for nitrogen. In Fig. 2, at the highest temperature, 658°, where there is relatively little hydrogen adsorbed on the catalyst, there is little or no deviation from a straight line (zero order test), but at the lower temperatures, 566 and 507°, the deviation is very marked; since the effect of hydrogen in slowing up the reaction increases with a decrease in temperature, it may constitute the entire difficulty in determining the order of the reaction. Further tests are under way to clear up this point.

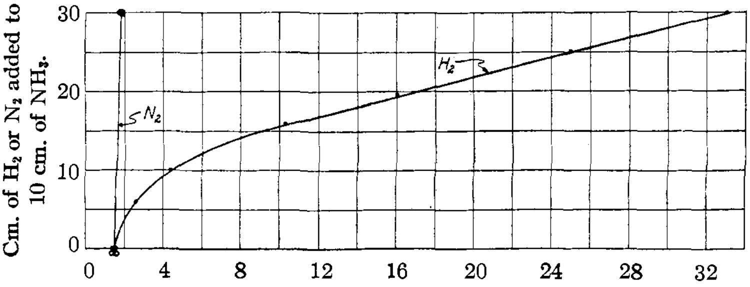

Fig. 3.—The effect of nitrogen and hydrogen on the rate of decomposition of ammonia on a catalyst surface at 630° (Fe–Al–K catalyst).

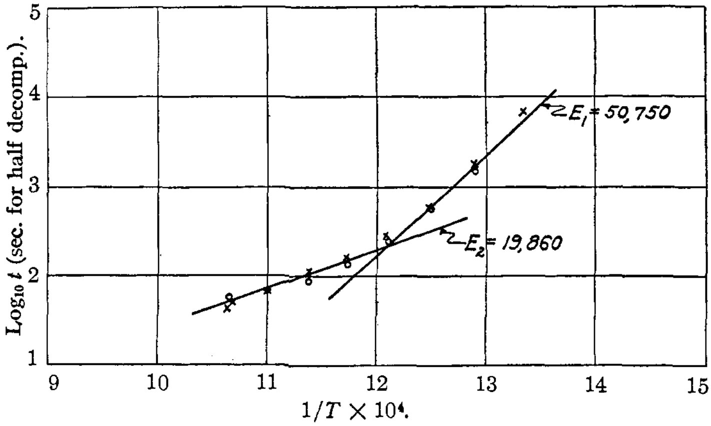

Fig. 4.—The temperature coefficient of the decomposition of ammonia on a catalyst surface (Fe–Al–K catalyst).

Determination of E.—The decomposition results will again be expressed in terms of Arrhenius' equation, rate of decomposition = $Ae^{-E/RT}$, where E will be determined from the temperature coefficient of the surface reaction as a function of the temperature. It is more obvious from Fig. 4 than in the previous work that a smooth curve drawn through all of the points will best represent the observed results, but again we will approximate the data by straight lines representing the range for values of E. Fig. 4 represents the data obtained from the surface when the activity of the surface had become constant after reduction. In this case an unreduced catalyst was coated and then reduced at a relatively low temperature. The test was taken by going from the high to the low temperature; the crosses represent these data, while circles represent the point obtained as the temperature was then increased. The failure of the two curves to be identical represents the effect of some change in surface. Fig. 5 (a) shows the results of a curve taken from one-fourth decomposition for the same test as Fig. 4, in comparison to the other curve, Fig. 5 (b), taken after four months of experiments on the same filament. The values of E and general form of the curve are the same but a considerable shift to a higher temperature range or lower catalytic activity was observed.

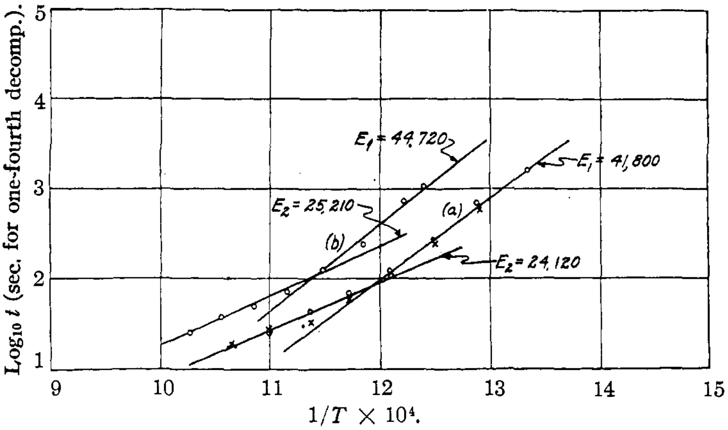

Fig. 5.—The temperature coefficient of the decomposition of ammonia on a catalyst, for (a) "1/4 time" and (b) "1/2 time" (Fe–Al–K catalyst).

The limit for the temperature range of the tests is determined by the length of the decomposition run. It was inconvenient to keep conditions constant over more than about five hours, time for half decomposition at the lowest rates, or to measure rates accurately at high temperatures where the time for half decomposition was less than a few minutes.

Promoters, Poisons and Heat Treatment Studies.—The results shown in Fig. 6 were taken considerably earlier and in a system somewhat different from that giving the other results. The four coated strips, about 10 cm. long and 1 mm. diameter, were mounted horizontally in a two-liter bulb. An effort was made to duplicate the method of coating, keeping the area of all the surfaces as nearly as possible the same. (a), (b) and (c) were mixtures that were first reduced and mixed with paraffin and flashed or coated at about 1000°. (a)[4] was a mixture containing the oxides of Fe–Al–Sn. (b) was a good grade of iron prepared in the form of a catalyst. (c) was one of the best catalysts developed for the synthesis of ammonia, being doubly promoted and containing Fe–Al–K. (d) was the same catalyst mixture as (c), Fe–Al–K, but was powdered, mixed with paraffin and coated in the unreduced form at about 350°. This Fe–Al–K oxide mixture was first thoroughly reduced in an atmosphere of $N_2 + 3H_2$ mixture before being used. The results are in general agreement with their relative activity in the synthesis of ammonia,[5] but, due to the very different conditions as to pressure and method in the synthesis and decomposition, nothing more than a relative comparison can be made. Tin is a very bad poison for a catalyst in the synthesis of ammonia and shows up as having the lowest activity in the decomposition. In comparison to (b), which is a straight iron catalyst, we may say that the tin has the effect of decreasing the rate of decomposition. On the other hand, the Al–K oxide promoter gives a more active catalyst than (b). The relative activity of (d) to (c) is due, undoubtedly, largely to the freedom of sintering in (d) caused by the difference in the method of coating. In this case a 10-fold increase in activity is observed at 527° of (d) over (c).

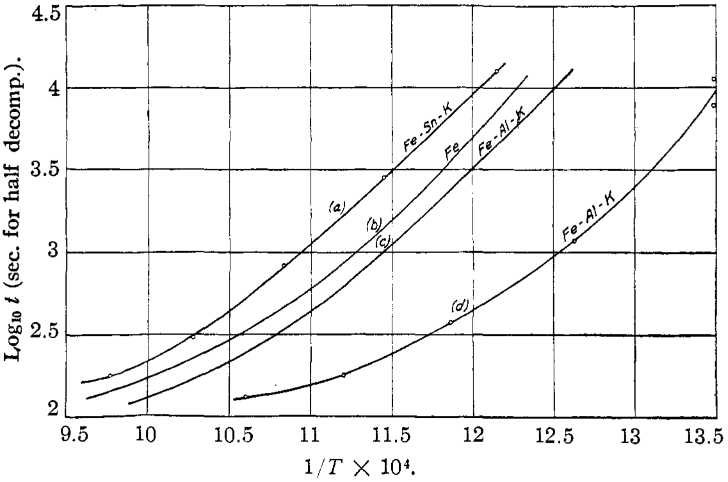

Fig. 6.—The effect of a promoter, poison and heat treatment on the rate of decomposition of ammonia on a catalyst surface.

All curves are of the same general nature, being displaced according to temperature alone. The effect of a promotor and low temperature coating

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[4] Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

[5] Almquist and Crittenden, *ibid.*, **18**, 1307 (1926); Larson and Brooks, *ibid.*, **18**, 1305 (1926).

is to displace the activity curve toward a lower temperature, while the effect of a poison is to displace the curve toward a higher temperature. These curves, including a difference of 16-fold activity at a given temperature, lead one to conclude that again the *A* or surface constant is of prime importance in determining the relative catalytic activity of these surfaces; that is, the effect of a promoter or poison is to increase or decrease, respectively, the amount of active surface or parts of the surface upon which the decomposition may take place, and is in accord with previous operations on these catalysts.[6]

Figure 7 gives for comparison the relative activity per sq. cm. for the various surfaces tested to date. The catalyst surfaces were determined from careful measurements of the diameter and length of the coated strips.

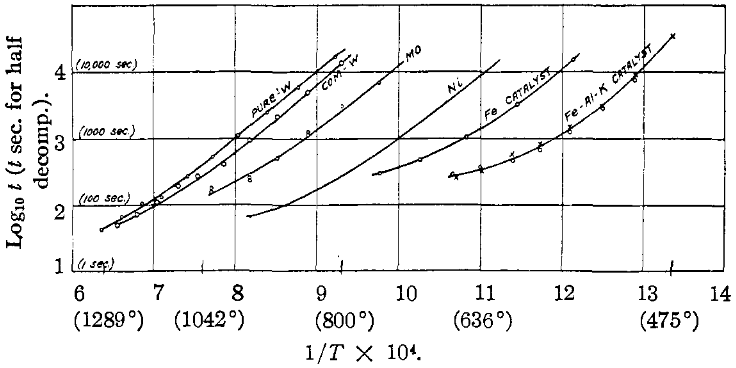

Fig. 7.—The relative activity of metal catalysts per square centimeter of surface for the decomposition of ammonia.

This method was used in the absence of a better method of comparison. These coated strips have more irregular surfaces than the drawn filaments previously tested. It appears from a careful inspection that all coated catalyst surfaces have about the same degree of roughness or irregularity and can therefore be dealt with as having about the same surface exposed to the ammonia gas. An effort was made to determine the activity of a drawn iron filament similar to nickel but without success. Due to bright spots resulting in an uneven temperature and the like, no complete run was obtained. From some individual tests we conclude that the iron curve would come close to the nickel curve.

We notice these marked similarities in all curves; first, that no single straight line will represent the data for an entire temperature range; second, that the more active the catalyst, the more marked deviation from a straight line, or the larger the variation in *E* with temperature. Drs. W. E. Deming and P. H. Emmett of this Laboratory have recently shown that

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[6] Almquist, THIS JOURNAL, **48**, 2820 (1926).

with an increasing adsorption of the products accompanying a decrease in temperature, less surface will be available for decomposition and that the relation between E and T will be a curve similar to the observed graph, Fig. 6, and not a straight line relation. These results will be published later.

The author wishes to express his appreciation to Dr. F. G. Cottrell, Director of the Laboratory, for suggestions and encouragement in this work; to Dr. E. D. Crittenden for valuable assistance in the early stages of the work; to Dr. P. H. Emmett for criticisms of this paper; to Mr. E. S. Lamar for assistance in the experimental work, and especially to Mr. R. A. Nelson for construction of apparatus and assistance throughout these studies.

Summary

The decomposition of ammonia on catalyst surfaces coated on platinum has been investigated and the results have been expressed and interpreted in terms of Arrhenius' equation. The data show that both the A and the E constants vary with temperature for a given catalyst.

The order of the reaction is not a simple one, on account of the retarding effect of hydrogen. The effect of hydrogen varies with the temperature of the catalyst, being small at the higher temperatures but large at the lower temperatures. Nitrogen has no appreciable effect on the rate.

The value of E as determined from the temperature coefficient varies from about 50,000 at the lower temperatures to 20,000 at the higher temperatures.

The effect of a promoter, poison or heat treatment of the surface is to displace the activity curve toward a lower or higher temperature, respectively, without any appreciable change in the form of the curve.

A summary of all of the surfaces tested shows that not only is the metal or mixture important, but of equal or more importance is the method of preparation of the catalyst surface and the heat treatment of the surface.

The results obtained indicate that no simple or easily interpretable meaning can be given to A or E, whereby the exact role played by the catalyst can be determined.

Tests are now in progress, the results of which promise to permit of a rigorous kinetic treatment.

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