which were found to vitrify, each possessed an asymmetric carbon atom, and only those five possessed an asymmetric carbon, which suggests that their vitrification may have been due to the presence of optical isomers. The cause of vitrification here would thus be analogous to the reason proposed for the vitrification of 1,2-dichloroisobutane, that is, the coexistence of different molecular forms. The vitrification or crystallization of the substances discussed in this paper is consistent with the guiding principles and tendencies previously discussed, but it is evident that a small difference in the size or the field of an atom or group in the molecule may greatly alter the tendency to vitrify.

Summary

The dielectric constants and specific conductances of i-butyl chloride, i-amyl chloride, t-amyl chloride, and 1,2-dichloroisobutane have been measured over a wide range of temperature at frequencies of 0.5, 5 and 50 kilocycles. The substances have also been observed over a wide range of temperature with a polarizing microscope.

The molecules of all four substances are too unsymmetrical to rotate in the crystalline state. t-Amyl chloride shows pronounced supercooling and i-amyl chloride very great supercooling. i-Butyl chloride vitrifies, but crystallizes at an intermediate temperature after long standing at liquid air temperature. 1,2-Dichloroisobutane vitrifies and shows only slight crystallization after prolonged thermal treatment.

The solid transition of 2,2-dimethylbutane has been found, by means of the polarizing microscope, to be enantiotropic, the high temperature form being isotropic and the low anisotropic. This, together with the high entropy of transition and low entropy of fusion, points to molecular rotation in the isotropic form.

The tendencies of these substances to crystallize or vitrify are compared with those of other alkyl halides and hydrocarbons. Some irregularity of molecular form and the possible coexistence of two or more molecular shapes contribute toward a tendency to vitrification. A small difference in the size of an atom or group in a molecule may make a large difference in the tendency to vitrify.

The Effect of Alkali Promoter Concentration on the Decomposition of Ammonia Over Doubly Promoted Iron Catalysts*

BY KATHARINE S. LOVE AND STEPHEN BRUNAUER

One of the many interesting unsolved problems of catalysis is the nature of the action of the alkali promoter in a doubly promoted iron synthetic ammonia catalyst. There is no doubt about the fact that the aluminum oxide promoter helps to create and maintain a large surface, since the total surface of singly promoted catalyst 954 (containing 10.2% aluminum oxide) is at least six times as large as that of a carefully reduced sample of pure iron catalyst 973. After continued operation at 450° the difference in surface becomes twentyfold.[1] However, the potassium oxide promoter showed no such surface enlarging action. It was pointed out by Emmett and Brunauer[2] that the total surface of catalyst 954 is about three times as large as that of doubly promoted catalyst 931

(containing 1.3% aluminum oxide and 1.6% potassium oxide), and yet the doubly promoted catalyst has a considerably greater activity toward the synthesis of ammonia at high pressures than the singly promoted catalyst. If one determines the number of iron atoms on the surface of these catalysts by chemisorption experiments[1,2,3] one finds that catalyst 954 has almost five times as many iron atoms on the surface as catalyst 931. It seems, therefore, that the alkali on the surface has some specific activating action on the neighboring iron atoms.

The kinetics of ammonia decomposition over catalyst 931 was calculated by Brunauer, Love and Keenan[4] from adsorption data. In their treatment of the problem the tacit assumption was made that every iron atom that is capable of chem-

* Not copyrighted.

(1) Emmett and Brunauer, THIS JOURNAL, 59, 1553 (1937).

(2) Emmett and Brunauer, ibid., 59, 310 (1937).

(3) Brunauer and Emmett, ibid., 62, 1732 (1940).

(4) Brunauer, Love and Keenan, ibid., to be published.

isorbing nitrogen is also capable of decomposing ammonia. Brunauer and Emmett[3] showed that the number of atoms of nitrogen chemisorbed by catalyst 931 is approximately equal to the number of iron atoms on the surface. It follows therefore that almost every iron atom of the surface is capable of decomposing ammonia. This is in good agreement with their conclusion that on the surface of catalyst 931 the iron atoms are so intimately mixed with the alkali promoter that almost every iron atom of the surface has an alkali molecule for its neighbor.

The alkali promoter thus has two antagonistic effects on the activity of the catalyst: it decreases the total surface and the number of iron atoms on the surface, but at the same time increases the activity of the neighboring iron atoms. One would expect, consequently, that at low alkali concentrations there would be a large catalyst surface but only a small number of the iron atoms would be activated by the promoter, whereas, at high alkali concentrations, most of the iron atoms on the surface would be active, but there would be a smaller number of them per unit weight of the catalyst. There should be, therefore, an optimum promoter concentration somewhere between these two extremes.

The work of Love and Emmett[5] showed that catalysts 954 and 931 exhibit very different kinetic behavior toward the decomposition of ammonia in the temperature range 380–440°. This reaction seemed, therefore, ideal for the study of the optimum alkali promoter concentration. A series of doubly promoted catalysts was prepared by soaking samples of the same singly promoted Fe_3O_4 catalyst in potassium hydroxide solutions of varying concentrations. After reduction, the rate of ammonia decomposition over each catalyst was measured, and the total surface and the concentrations of the promoters on the surface of each catalyst were determined. The purpose of these experiments was to obtain some correlation between the surface concentrations of the alkali promotor and the mechanism of ammonia decomposition over the same catalysts.

Experimental

Singly promoted iron synthetic ammonia catalyst 191 (0.42% Al_2O_3) was chosen as the base from which the series of doubly promoted catalysts was prepared. Samples of catalyst 191 were soaked in potassium hydroxide solutions of varying strength, drained by suction, and dried at 120°. Table I, Column 2, gives the strength of the potassium hydroxide solutions used. The catalysts thus prepared were analyzed for potassium oxide content, and Column 4 gives the results of the analyses. Only the untreated catalyst was analyzed for aluminum oxide (Column 3). Since it is a well known fact that the aluminum oxide promoter forms a solid solution with the Fe_3O_4 catalyst, it seems safe to assume that the potassium hydroxide treatment had no appreciable influence on the aluminum oxide content of the prepared catalysts.

For comparison with the series described above, we have also investigated two regular doubly promoted catalysts, 441 and 931. These catalysts were originally prepared by melting the Fe_3O_4 catalyst in an electric furnace and adding *both* promoters to the molten oxide. The promoter contents of these catalysts are given in Columns 3 and 4.

The catalyst chamber of the apparatus was so arranged that by turning a stopcock it could be connected to (1) an adsorption apparatus for measuring the total surface and the concentrations of the promoters on the surface of the catalyst, (2) an apparatus for determining the rate of ammonia decomposition over the catalyst. The adsorption apparatus and experimental technique were similar to those described by Emmett and Brunauer,[6] while the apparatus and technique for the study of the ammonia decomposition were the same as those used by Love and Emmett.[5]

In the experiments, 1.5 cc. of catalyst was placed in the catalyst chamber and reduced with a flow of about 240 cc. of hydrogen per minute for twenty-four hours at 400°, forty-four hours at 450°, and twenty-four hours at 500°. The total surface of the catalyst was then measured by determining a van der Waals adsorption isotherm of nitrogen at −183°.[1] This was followed by measurements of the rate of ammonia decomposition at three temperatures: at approximately 395, 440 and 475°. At each temperature the rate was determined with two gas compositions: one consisting of a flow of 315 cc. of hydrogen and 45 cc. of ammonia per minute, the other of 225 cc. of hydrogen, 90 cc. of nitrogen and 45 cc. of ammonia per minute.

Each of the rate determinations was the result of a day's run. The catalyst was first reduced for at least one hour with pure hydrogen at the temperature of the run. Then either ammonia or the ammonia–nitrogen mixture was turned into the hydrogen stream and the reaction was allowed to continue for three hours before the rate readings were made. It was found in the previous work[5] with catalysts 931 and 954 that this was ample time for the reaction to reach steady state. The rates reported in the present work represent averages of two or three rate readings.

After the completion of the rate determinations at three different temperatures and two different gas compositions, the total surface was again measured by nitrogen adsorption, and then the concentrations of the promoters on the surface of the catalyst were determined by measuring the chemisorptions of carbon monoxide and carbon dioxide at −78°.[1,3] These experiments concluded the investigation for most of the catalysts. On a few catalysts further ammonia decomposition runs were made at other temperatures after the chemisorption experiments.

(5) Love and Emmett, THIS JOURNAL, **63**, 3297 (1941).

(6) Emmett and Brunauer, *ibid.*, **56**, 35 (1934).

TABLE I

CHEMICAL ANALYSIS AND ADSORPTION DATA

Cat. No.	Strength of soln., % K_2O	Catalyst data Promoter content of catalyst, % Al_2O_3	K_2O	Unreduced sample, g.	Adsorption data N_2 ads. at $-183°$, 200 mm. per g. cat., cc., S. T. P.	Chemisorbed at $-78°$ per g. cat., cc., S.T.P. CO_2	CO	Surface composition % of surface covered by Alkali	Fe	Free Al_2O_3
191	..	0.42	..	3.53	1.33	..	1.08[a]	...	65	35
191-A	2	.42[b]	0.09	3.65	1.36	0.22	0.93	16	55	29
191-B	5	.42[b]	.18	3.53	1.23	.28	.78	23	51	26
191-C	7.5	.42[b]	.25	3.56	1.28	.40	.72	31	45	24
191-D	10	.42[b]	.44	3.53	1.05	.41	.52	39	40	21
191-E	15	.42[b]	..	3.49	1.06	.44	.56	42	42	16
441	..	.84	.35	3.39	1.27	.49	.76	38	48	14
931	..	1.30	1.59	3.47	0.50[c]	..	..	60[c]	40[c]	0[c]

[a] Estimated from measurement made after final kinetic run.   [b] Assumed to be the same as that of catalyst 191.
[c] Taken from measurements of Brunauer and Emmett[3] made on another sample of catalyst 931.

Results

The results of the adsorption experiments are summarized in Table I. Column 6 gives the volume of nitrogen adsorbed per gram of catalyst at $-183°$ and 200 mm. pressure. This is approximately equal to the volume of nitrogen necessary to cover the entire surface of 1 g. of catalyst with a unimolecular adsorbed layer. A comparison of the nitrogen adsorption values of Column 6 gives the relative surfaces of the catalysts investigated with an uncertainty that is less than 5%. The nitrogen values represent the surface determinations after the six kinetic runs, with the exception of that given for catalyst 931, which was taken from the data of Brunauer and Emmett.[3]

The total surface measurements made on the catalysts between the initial reduction and the first ammonia decomposition run are not given in the table. There was very little sintering observed during the six kinetic runs. The greatest change was observed for catalyst 191, which had a nitrogen adsorption of 1.38 cc./g. after the reduction and 1.33 cc./g. after the six runs.

The concentrations of the potassium oxide and aluminum oxide promoters on the surfaces of the catalysts were calculated from the chemisorption measurements of carbon dioxide and carbon monoxide at $-78°$, given in Columns 7 and 8. All of these measurements were made after the six decomposition runs except the chemisorption of carbon monoxide on catalyst 191. On this catalyst a large number of decomposition runs were made, and the chemisorption was determined only after the last run. However, Brunauer and Emmett[3] found that in the case of the singly promoted catalyst 954 the ratio of carbon monoxide chemisorption to the van der Waals nitrogen adsorption remained constant as the catalyst progressively sintered. Since it is very likely that catalyst 191 behaves in this respect in the same manner, one could estimate without difficulty the chemisorption after the six runs.

It was found by Emmett and Brunauer[1,2,3] that the chemisorption of carbon dioxide occurs almost exclusively on the alkali molecules of the surface, whereas the chemisorption of carbon monoxide takes place only on the iron atoms of the surface. Since chemisorbed carbon monoxide is about 25% more densely packed on the surface than van der Waals nitrogen, one can obtain the fraction of the surface covered with iron atoms by dividing 80% of the carbon monoxide chemisorption by the nitrogen adsorption of Column 6. The ratio of the carbon dioxide chemisorption to the nitrogen adsorption gives the fraction of the surface covered with alkali molecules. There is considerable evidence that the alkali on the surface of some doubly promoted catalysts is not free potassium oxide but a complex between potassium oxide and aluminum oxide, possibly potassium aluminate.[3] The sum of the iron and alkali fractions subtracted from 1 gives the fraction covered by the free aluminum oxide promoter. The results for the fractions of the surface covered by alkali, iron, and free aluminum oxide evaluated in this manner are given in the last three columns of Table I.

The results of the ammonia decomposition are shown in Figs. 1, 2, and 3. The data are plotted according to the Arrhenius equation, i. e., the logarithm of the rate of decomposition is plotted against the reciprocal of the absolute temperature. The slopes of such curves give the apparent energies of activation. There are two curves for
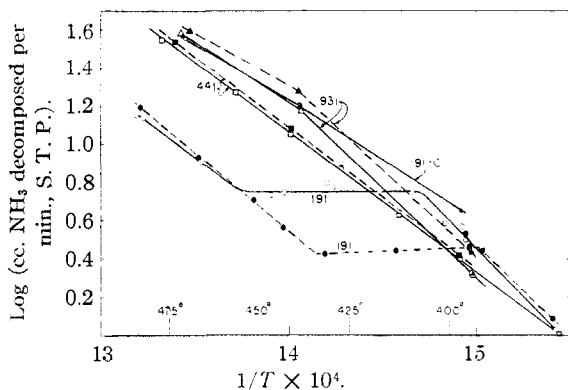
Fig. 1.—Temperature dependence of the rate of ammonia decomposition over catalysts 191, 191-C, 441 and 931: O, o, □, △ data obtained with a flow of 315 cc. of hydrogen and 45 cc. of ammonia per min.; ●, •, ■, ▲, data obtained with a flow of 225 cc. of hydrogen, 90 cc. of nitrogen and 45 cc. of ammonia per min.; O, ●, catalyst 191; o, •, catalyst 191-C; □, ■, catalyst 441; △, ▲, catalyst 931.

each catalyst corresponding to the two different gas compositions used. The continuous curves were obtained with a flow of 315 cc. of hydrogen and 45 cc. of ammonia per minute, the broken curves with a flow of 225 cc. of hydrogen, 90 cc. of nitrogen, and 45 cc. of ammonia per minute.

In Fig. 1 the rates of decomposition of ammonia over singly promoted catalyst 191 are compared with the rates over two doubly promoted catalysts, 441 and 931. In Figs. 2 and 3 the ammonia decomposition data are shown for catalyst 191 and the series of doubly promoted catalysts prepared from it. Logically these data all should be on the same graph, but it is easy to see that this would lead to a hopelessly confusing mass of experimental points and crossing curves. The curves for catalyst 191 are repeated in all three figures to facilitate comparison.

Discussion

An examination of the data for catalyst 191 and the series prepared from it, in Table I, leads to the following conclusions:

(1) The total surface of the catalyst decreases with increasing alkali promoter content. As little as 0.1% potassium oxide does not affect the total surface. With 0.2% potassium oxide there is a very slight decrease, almost on the borderline of the experimental error. A promoter content of about 0.4% leads to a decrease of about 20-25%.

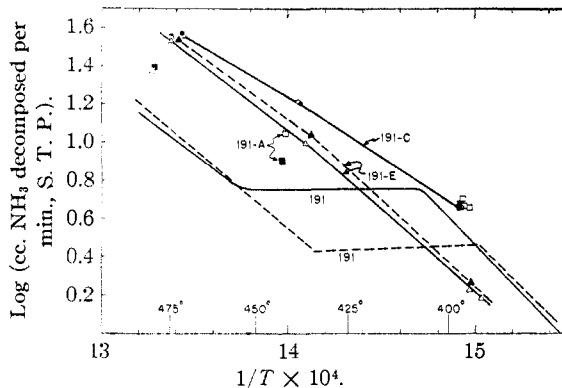(2) The fraction of the surface covered by alkali increases with increasing alkali promoter content.

Fig. 2.—Temperature dependence of the rate of ammonia decomposition over catalysts 191, 191-A, 191-C and 191-E: □, o, △, data obtained with a flow of 315 cc. of hydrogen and 45 cc. of ammonia per min.; ■, •, ▲, data obtained with a flow of 225 cc. of hydrogen, 90 cc. of nitrogen and 45 cc. of ammonia per min.; □, ■, catalyst 191-A; o, •, catalyst 191-C; △, ▲, catalyst 191-E.
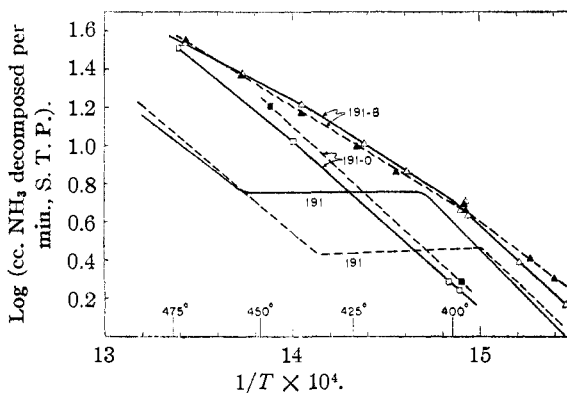

Fig. 3.—Temperature dependence of the rate of ammonia decomposition over catalysts 191, 191-B and 191-D: △, □, data obtained with a flow of 315 cc. of hydrogen and 45 cc. of ammonia per min.; ▲, ■, data obtained with a flow of 225 cc. of hydrogen, 90 cc. of nitrogen and 45 cc. of ammonia per min.; △, ▲, catalyst 191-B; □, ■, catalyst 191-D.

(3) The fractions of the surface covered by iron and free aluminum oxide decrease with increasing alkali promoter content. The iron and aluminum oxide fractions decrease in the same proportion. The ratio of the iron fraction to the aluminum oxide fraction is 1.9 for catalyst 191, and it remains the same for catalysts 191-A, B, C, and D. Thus the alkali promoter has no preference for either iron or aluminum oxide on the surface; as it accumulates on the surface, it covers up the iron and the aluminum oxide at random. Catalyst 191-E appears to be an exception, more aluminum oxide than iron seems to be covered by potassium oxide. Only further experiments could decide whether this observation is due to experi-

mental error or to a real change in the manner in which the alkali goes on the surface.

Love and Emmett[5] found that doubly promoted catalyst 931 differed very markedly from singly promoted catalyst 954 in its behavior toward the decomposition of ammonia. The Arrhenius plots were straight lines for catalyst 931 throughout the entire temperature range investigated (from about 350 to about 440°), indicating a constant apparent energy of activation of about 44,000 calories per mole.[7] The rate of decomposition for the entire temperature range could be expressed by the kinetic equation

$$\frac{-dP_{NH_3}}{dt} = k\frac{P_{NH_3}^{0.60}}{P_{H_2}^{0.85}}$$

On the other hand, catalyst 954 showed no constancy either in the apparent energy of activation or in the kinetic equation for the same temperature range. The Arrhenius plots showed three distinct regions. In the middle region the apparent energy of activation was approximately zero, and the kinetic equation was reversed: hydrogen did not inhibit but promoted the decomposition, and ammonia inhibited it. In the higher and lower temperature regions both the energy of activation and the kinetic expression approached those of the reaction over catalyst 931.

Figure 1 illustrates that other typical singly and doubly promoted catalysts than 954 and 931 show very similar behavior to those two catalysts. Doubly promoted catalyst 441 shows a constant apparent energy of activation throughout the entire temperature range, just like catalyst 931. The two straight lines, corresponding to the two different gas compositions, run nearly parallel, the one having the higher hydrogen partial pressure giving a lower rate of decomposition, showing that hydrogen inhibits the reaction. Singly promoted catalyst 191 shows three distinct regions, just like catalyst 954. The middle region shows approximately zero energy of activation and reversed kinetic equation, i. e., hydrogen promotes the decomposition. The high and low temperature regions also show the same characteristics as were found for catalyst 954; large apparent energies of activation and normal kinetic behavior, i. e., inhibition by hydrogen.

Figure 1 also includes two curves obtained for

(7) This value was not corrected for the change in the composition of the gas mixture as it passes over the catalyst. The correction raises the energy of activation for catalyst 931 by about 2000 calories. All the points in the three figures of the present paper represent uncorrected rate values.

the decomposition of ammonia over another sample of doubly promoted catalyst 931. The bend in the curves at higher temperatures is probably due to the large decomposition of ammonia. Love and Emmett[5] chose the sizes of their samples of catalyst 931 so that the decomposition was small, and the change in the composition of the gas as it passed over the catalyst was slight. In the present experiments one sample of the catalyst was used at all temperatures. At 470° the decomposition was so large that the partial pressure of ammonia at the exit was only one-seventh of the entering partial pressure. Since the rate of decomposition is proportional to $P_{NH_3}^{0.60}$, one would expect a large drop in the rate as the gas passes through the catalyst.

Figures 2 and 3 show the change in the kinetic behavior of catalyst 191 as more and more alkali is added to it. As alkali accumulates on the surface of this catalyst, the kinetics of ammonia decomposition shift more and more toward the kinetics characteristic of catalyst 931.

The data obtained for catalyst 191-A (Fig. 2) are not sufficient to draw the curves, consequently the experiments are indicated as isolated points. It should be noted that this catalyst, having 16% of its surface covered by alkali, still behaves very much like a singly promoted catalyst, it still shows the reversed kinetics in the middle region, i. e., promotion by hydrogen instead of inhibition. However, the activating influence of the alkali molecules is clearly observable, the rate of decomposition is much higher at all temperatures studied than the rate over catalyst 191.

Catalyst 191-B (Fig. 3) shows a further shift in the direction of doubly promoted catalyst 931. This catalyst has 23% of its surface covered by alkali, and yet shows some remnants of the characteristics of a singly promoted catalyst. The two curves corresponding to the two different gas compositions still cross each other twice, but in the middle region there is only a very slight promotion by hydrogen. There is a further increase in the reaction rate: at 450° it is now about three and a half times as fast as that over catalyst 191.

Catalyst 191-C (Fig. 2) seems to lie on the borderline between singly promoted catalysts 954 or 191 on the one hand and doubly promoted catalyst 931 on the other. This catalyst has 31% of its surface covered by alkali. The two different gas compositions now give the same rate curve.

There is neither inhibition nor promotion by hydrogen; the rate appears to be of zero order with respect to hydrogen. The curve lies just between the two curves of catalyst 191-B (Fig. 3), except around 475° where it rises above them. It should be also noted that the rate at 400° over this catalyst is higher than the rate over catalyst 191 at that temperature. The total surface is still about as large as the surface of catalyst 191. The next catalyst of the series shows already a definite decrease in the total surface and the rate at 400°, and a kinetic equation characteristic of doubly promoted catalyst 931.

The last two catalysts, 191-D (Fig. 3), containing 39% alkali on its surface, and 191-E (Fig. 2), containing 42% alkali on its surface, behave like catalyst 931. The apparent energy of activation is almost constant; whatever bend there is in the curves, is probably due to the large decomposition at higher temperatures. Hydrogen inhibits the reaction throughout the entire temperature range. The total surface is lower by 20–25% than that of catalyst 191.

It is of considerable interest to note the similarity between the behavior of the catalysts of the 191 series and the doubly promoted catalyst 441. The latter is a very active synthetic ammonia catalyst made in the usual manner by adding the alkali along with the aluminum oxide promoter to the molten Fe_3O_4. The potassium oxide content of this catalyst falls between the alkali contents of catalysts 191-C and D, as Table I, Column 4 shows. The percentage of the surface covered by alkali also falls between the values given for catalysts 191-C and D, in Column 9. Very interestingly the kinetic behavior of catalyst 441 is also intermediate between that of catalysts 191-C and D. The apparent energy of activation over catalyst 191-C is about 29 kcal., that over 191-D is about 41 kcal., whereas that over catalyst 441 is about 34 kcal. The rate of ammonia decomposition is independent of the partial pressure of hydrogen for catalyst 191-C, varies inversely as $P_{H_2}^{0.47}$ for catalyst 191-D and inversely as $P_{H_2}^{0.15}$ for catalyst 441.

Catalyst 441 has a larger aluminum oxide content than the catalysts of the 191 series, as Table I, Column 3 shows. This fact, however, does not seem to influence very markedly either the composition of the surface, or the kinetics of the ammonia decomposition. Even the total surface of catalyst 441 falls between those of catalysts 191-C

and D, although perhaps it is slightly larger than one would expect for a catalyst of the 191 series having the same alkali content. This is probably due to the larger aluminum oxide content.

The similarity between the behavior of catalyst 441 and the catalysts of the 191 series leads to the conclusion that it does not make much difference as far as the decomposition of ammonia is concerned whether the potassium oxide promoter is added to the molten Fe_3O_4 catalyst at high temperatures along with aluminum oxide, or is added to the singly promoted catalyst at room temperature in the form of a potassium hydroxide solution. The latter procedure probably enables one to control more accurately the potassium oxide promoter content of the catalyst.

Catalyst 931 is an extreme case of the doubly promoted catalyst. Its alkali promoter content is much higher than that of any of the other catalysts studied, and the surface concentration of alkali is also correspondingly higher. The total surface is much smaller than that of the other catalysts. The apparent energy of activation is the largest, about 44,000 calories per mole, and the inhibition by hydrogen is the greatest, i. e., the rate is inversely proportional to $P_{H_2}^{0.85}$.

The results of the present work indicate that for the ammonia decomposition reaction there is an optimum potassium oxide promoter content for any given aluminum oxide content that can be ascertained by studies similar to ours. The most active catalysts of the 191 series were 191-B and C. Figure 1 shows a comparison between catalyst 191-C and the two doubly promoted catalysts 441 and 931. Clearly, catalyst 191-C is more active toward ammonia decomposition in the entire temperature range studied than catalyst 441, and is more active at lower temperatures than catalyst 931.

It would have been of great interest to vary the aluminum oxide promoter content also by preparing several other series from singly promoted catalysts of larger (and possibly of smaller) aluminum oxide content. However, various circumstances prevented the continuation of the present investigations.

Naturally, it would be of much greater practical importance to find the optimum promoter concentrations for the ammonia synthesis reaction. We believe that with careful control of the aluminum oxide and potassium oxide promoter contents a more active iron synthetic ammonia

catalyst could be developed than those we have at present.

Summary

In order to find the optimum alkali promoter concentration for iron synthetic ammonia catalysts, a series of doubly promoted catalysts was prepared by treating an aluminum oxide promoted catalyst with potassium hydroxide solutions of varying strengths. By adsorption measurements the total surface areas and the surface concentrations of the promoters were determined for each catalyst, and the effects of temperature and gas composition on the kinetics of ammonia decomposition were investigated. The most active catalyst toward ammonia decomposition was obtained when about 30% of the catalyst surface was covered by the alkali promoter.

Adsorption of Nitrogen and the Mechanism of Ammonia Decomposition Over Iron Catalysts*

BY STEPHEN BRUNAUER, KATHARINF S. LOVE AND ROBERT G. KEENAN

Since Taylor[1] advanced the concept of activated adsorption, a number of attempts have been made to show that adsorption and desorption processes constitute the rate determining step in certain catalytic reactions. One of the most interesting among these attempts is a recent theoretical treatment of the decomposition of ammonia that was proposed by Temkin and Pyzhev.[2] They adopted the conventional idea that the rate determining step was the desorption of nitrogen molecules from the surface but in their treatment of the problem they introduced a novel assumption. They discarded the generally held concept that the rate of desorption varies linearly with the fraction of the surface covered by adsorbed gas and assumed instead an exponential relationship, originally proposed by Langmuir[3]

$$w = k_d e^{h\theta} \qquad (1)$$

where w is the rate of desorption, θ is the fraction of the surface covered with adsorbed gas, and k_d and h are constants. A corresponding equation for the rate of adsorption was first obtained by Zeldowitsch.[4]

$$z = k_a p e^{-g\theta} \qquad (2)$$

where z is the rate of adsorption, p is the pressure, and k_a and g are constants. Although these two equations were applied with success to a few cases of adsorption and desorption, it is obvious that

Eq. (1) breaks down for low values of θ and Eq. (2) for high values of θ. The rate of adsorption should be zero when $\theta = 1$, and the rate of desorption should be zero when $\theta = 0$. These conditions are not fulfilled by the two equations.

At equilibrium the rate of adsorption is equal to the rate of desorption. If one equates (1) and (2), one obtains the adsorption isotherm equation

$$\theta = (1/f) \ln a_0 p \qquad (3)$$

where f and a_0 are constants. This equation was first published by Frumkin and Slygin,[5] who credited Temkin with its derivation, but to our best knowledge the derivation has not been published to date. Equation (3) is not valid for either small or large adsorptions since it does not reduce to $\theta = 0$ for $p = 0$, nor to $\theta = 1$ for very large values of p. It is valid only in the middle range of adsorption, as will be shown later.

If the slow step in the decomposition of ammonia over iron catalysts is the rate of escape of nitrogen from the surface, then the rate of desorption as given by (1) can express the rate of ammonia decomposition. In this case θ is the fraction of the surface covered by adsorbed nitrogen. The value of θ is obtained from Eq. (3). Substituting (3) into (1), we get

$$-\frac{dP_{NH_3}}{dt} = w = k_d e^{(h/f) \ln a_0 p} \qquad (4)$$

In the calculation of p, the equilibrium pressure of nitrogen, Temkin and Pyzhev adopted the assumption of Winter,[6] namely, that the amount of nitrogen on the surface is determined by the

* A part of this paper is from the thesis of Robert G. Keenan, presented to the Faculty of the George Washington University in part satisfaction of the requirements for the degree of Master of Science. Not copyrighted.

(1) Taylor, THIS JOURNAL, **53**, 578 (1931).

(2) Temkin and Pyzhev, Acta Physicochim., U. R. S. S., **12**, 327 (1940).

(3) Langmuir, THIS JOURNAL, **54**, 2798 (1932).

(4) Zeldowitsch, Acta Physicochim., U. R. S. S., **1**, 449 (1934).

(5) Frumkin and Slygin, ibid., **3**, 791 (1935).

(6) Winter, Z. phys. Chem., **B13**, 401 (1931).