The relation of the above observations to the nature of the catalyst surface and the effect of promoters will be discussed in the paper that follows.

Summary

A quantitative study has been made of the inhibiting effect of small concentrations of oxygen on the activity of several iron catalysts for ammonia synthesis. For all of the catalysts over the range of oxygen concentrations covered, there results a lowering of the ammonia concentration produced to a constant value. This final ammonia concentration is lower, the higher the oxygen concentration and for equal concentrations of oxygen is lower for the less active catalysts. The poisoning action is accompanied by the formation of some iron oxide, the quantity of which is greater for the more active promoted catalysts. The effects of equivalent concentrations of oxygen and water vapor are identical as regards the decrease of ammonia concentration and the formation of iron oxide on the catalyst.

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THE NATURE OF THE CATALYST SURFACE AND THE EFFECT OF PROMOTERS

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The concept of a reduced metal catalyst, now generally held, is that of a material which contains certain points of catalytic activity and that these points usually constitute a relatively small fraction of the total reduced metal sample.[1] The catalytic activity is resident in certain of the reduced metal atoms which, by virtue of their position with respect to neighboring metal atoms, possess unsaturated valence forces capable of effecting distortion of the gas molecules necessary for reaction. Thus, in a metal catalyst reduced from its oxide, there are present atoms varying in degree of unsaturation from that exhibited by atoms in the plane surface of the metal crystal lattice[2] to that of atoms which are held so loosely by neighboring atoms as to approach, according to Taylor[3] and Armstrong and Hilditch[4] the condition of a gaseous metal atom.

Evidence has also been obtained from poisoning experiments[5,6] which

[1] See for example, "Fourth Report of the Committee on Contact Catalysis," Taylor, *J. Phys. Chem.*, **30**, 145 (1926).

[2] Langmuir, THIS JOURNAL, **38,** 2249 (1916).

[3] Taylor, *Proc. Roy. Soc.*, **108A,** 105 (1925).

[4] Armstrong and Hilditch, *ibid.*, **108A,** 111 (1925).

[5] Vavon and Husson, *Compt. rend.*, **175,** 277 (1922).

[6] Kubota and Yoshikawa, *Sci. Papers Inst. Phys. Chem. Res.*, Japan, **3,** 223 (1925).

confirms this view of the inequality in the catalytic efficiency of the surface atoms. We do not, however, know how the catalytic activity for a given reaction is distributed among the unsaturated or active atoms or how the number of active atoms in a given catalyst compares with the total number of metal atoms present.

The ability of extremely small quantities of poisons to suppress the activity of reduced metal catalysts for many reactions is the chief reason why it has been necessary to postulate that only a relatively small part of the metal catalyst is active in catalysis. This suggests that a quantitative study of catalyst poisoning under suitable conditions should render possible the determination of the fraction of a given catalyst mass that has an appreciable part in the catalytic action. In the case of pure iron and promoted iron catalysts for ammonia synthesis, oxygen is the type of poison which seemed best suited for such a study, and the poisoning experiments described in the preceding paper[7] were carried out with this end in view, particularly as regards the effect of promoters.

In the light of our present knowledge of catalysts, the action of promoters in enhancing the activity of a given catalyst material may be attributed to their ability (1) to increase the number of active atoms or groups of atoms in a given quantity of catalyst or (2) to alter specifically the nature of the active atoms, rendering each capable of effecting a greater number of transformations in a given time. It is probable that both of these effects, one a quantity and the other a quality factor, are active in many cases of promoter action.

In the case of iron catalysts for ammonia synthesis, it has been shown by x-ray[8] and adsorption studies that one important function of the promoters alumina and potassium aluminate is the control of the reduced structure, so as to provide a more extensive surface. This, together with the observation of the preceding paper[7] that the active promoted catalysts are capable of retaining much more oxygen than a pure iron catalyst under the same conditions, indicates that the effect of such promoters is predominantly that of increasing the number of active atoms. All of the observations in the oxygen-poisoning study are in accord with this view, as may be seen from a comparison of Catalyst 918, pure iron, and No. 921, a typically active promoted catalyst.

On pure gas the greater activity of 921 over 918 may be attributed largely to the presence of a greater number of active atoms in the equal weight samples under test. In the tests on oxygen-containing gas, at 5000 space velocity, 918 shows an immediate drop because this particular rate of gas flow happens to be a critical one in the sense that this catalyst is just able to synthesize the equilibrium concentration of ammonia under

[7] Almquist and Black, THIS JOURNAL, **48**, 2814 (1926).

[8] Wyckoff and Crittenden, *ibid.*, **47**, 2866 (1925).

these conditions. Catalyst 921 on the other hand, is able to synthesize this equilibrium concentration at much higher rates of flow and hence the sample contains more active material than is required to produce equilibrium at 5000 space velocity. When exposed to oxygen, therefore, no drop in the ammonia concentration occurs until the number of the active atoms has been reduced by combination with oxygen, to the critical number actually required for the realization of equilibrium. Thereafter, the drop is rapid as in the case of 918. Experiments at other rates of flow than 5000 space velocity (s. v.) are in accord with this view. Thus, the more active catalysts (921 and 922) exhibit characteristics at 25,000 s. v. very similar to those shown by 918 at 5000 s. v., like concentrations of oxygen. Similarly, 918 at 1000 s. v. yields results quite like those for 921 and 922 at 5000 s. v.

The lag, therefore, in each case represents the time required for the accumulation of sufficient oxygen on the catalyst to reduce the number of active atoms to the critical number required for synthesizing the equilibrium concentration of ammonia under the conditions employed. From Fig. 4[7] it is seen that for Catalyst 921, this quantity of oxygen is nearly 5 mg. and is independent of the oxygen concentration.

It is interesting to see what can be done with the foregoing data in the way of estimating the degree of unsaturation of the active iron atoms and the ratio of the number of these active atoms to the total iron present in these catalysts. The results given in Table II of the preceding paper are the quantities of oxygen retained by the various catalysts after the steady state has been attained, and we also know the constant concentration of ammonia which each is capable of producing, after this quantity of oxide has been built up. Further, both the ability of the catalysts to synthesize ammonia and to form a stable oxide in the range of oxygen concentrations used must be a property of unsaturated atoms, since massive iron in the form of turnings has no appreciable activity in ammonia synthesis and is not oxidized by the highest concentration of oxygen in hydrogen, 0.24%, that was used. Since the effects of equivalent concentrations of oxygen and water vapor were found to be identical, a comparison of our observation on oxide formation may be made with the known results for the equilibrium in the system, iron—iron-oxides—water-vapor—hydrogen.

At 444° the stable oxide phase is Fe_3O_4 and from the extrapolated data of Eastman and Evans[9] the equilibrium for the reaction, $3/4Fe + H_2O = 1/4Fe_3O_4 + H_2$, is represented by $K = H_2/H_2O = 5$.

This is equivalent to a volume percentage of water vapor of about 16%. That is, iron at this temperature should not be oxidized by hydrogen-steam mixtures containing less than 16% of steam. In our experiments some oxidation of catalytic iron occurred at the lowest oxygen concentra-

[9] Eastman and Evans, THIS JOURNAL, **46,** 896 (1924).

tion used, namely 0.008%, which is equivalent to 0.016% of water vapor. At 0.02% of oxygen or 0.04% of water vapor, the oxidation corresponded to the retention of 4.8 mg. of oxygen, at the steady state, that is, after the water in the gas leaving the catalyst was equal to that entering.

The ratio of H_2/H_2O was then 75/0.04, for which $K = 1875$. While the ratio of these equilibrium constants may be taken as an approximate measure of the greater ease of oxidation of a certain range of unsaturated iron atoms, as compared to crystalline iron,[10] it must be recognized that the two constants are not strictly comparable in that we do not know what the solid oxide phase is in the latter case. Indeed, since the small number of unsaturated atoms undergoing oxidation is widely distributed among a large number of normal iron atoms, it would not be expected that a definite oxide phase such as Fe_3O_4 would be formed. On this basis, the variation in the equilibrium constants is a function of both solid phases, iron and iron oxide. If we make the assumption, however, that the solid oxide phases are the same, and that all of the change is attributed to a difference in the iron phase, it is possible to determine a maximum energy difference between crystalline iron and the average of the unsaturated atoms over the range covered, by combination of the equations:

$$^3/_4\,\mathrm{Fe} + \mathrm{H_2O} = {}^1/_4\,\mathrm{Fe_3O_4} + \mathrm{H_2};\ K_1 = 5 \qquad (1)$$

$$^3/_4\,\mathrm{Fe\ (active)} + \mathrm{H_2O} = {}^1/_4\,\mathrm{Fe_3O_4} + \mathrm{H_2};\ K_2 = 1875 \qquad (2)$$

By subtracting (1) from (2)

$$^3/_4\,\mathrm{Fe_{(a)}} = {}^3/_4\,\mathrm{Fe}\ (K_2/K_1) = 375 \qquad (3)$$

for which, at 444°, $\Delta F = -RT\,ln\,(K_2/K_1) = -8600$ cal., or —11,500 cal. per gram atom of iron. This value then represents an upper limit for the average free energy of a range of unsaturated iron atoms which are responsible for the greater part of the ammonia-synthesizing activity of the catalyst. A similar calculation employing the lowest concentration of water vapor used, namely 0.016%, gives an energy value of 13,200 cal. which is of the same order of magnitude. With reference to the equilibria involving iron oxides, the reactivity toward water vapor of unsaturated atoms suggests that their presence may supplement the explanation involving solid solution for the decrease in the H_2O/H_2 ratio, which has been observed at low concentrations of oxygen in the solid phase.[11]

In order to get a measure of the number of atoms capable of catalyzing ammonia formation from the quantity of oxygen retained, it is necessary to make the assumption that the same atoms are taking part in these two ef-

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[10] Compare Pease and Cook, This Journal, **48,** 1202 (1926). These investigators, in studying the equilibrium in the reaction $NiO + H_2 = Ni + H_2O$ by a dynamic method, observed that the yield of hydrogen obtained when steam is first passed over the reduced nickel was considerably higher than the equilibrium value finally attained. This manifestation of a greater initial activity toward steam of nickel reduced from its oxide is quite in accord with our observations on iron.

[11] See Eastman and Evans, *ibid.*, **46,** 892 (1924).

fects, that is, that the degree of activity or unsaturation required for ammonia formation is about the same as that necessary for the reaction with the low concentrations of water vapor used. Such an assumption is not entirely lacking in support, since we know that extremely small quantities of oxygen are able to lower a catalyst's ammonia-forming capacity, and further that all of our poisoning tests showed that no appreciable formation of oxide occurred after the concentration of ammonia produced had leveled off at a constant value. In other words, the fact that the steady states for the two reactions appear to be so nearly coincident indicates that all of the oxygen retained by the catalyst is held by atoms that would have some activity in ammonia formation if the oxygen were not there. If we assume in addition that the combination of oxygen and iron occurs in the ratio of one atom of oxygen to one of iron, we can calculate from the known weight of oxygen retained by a known weight of iron the ratio of total iron atoms to unsaturated or active atoms for both the pure iron and the promoted iron catalysts. Such calculations for various oxygen concentrations and hence for different degrees of poisoning are given in Table I.

TABLE I

RATIO OF ACTIVE IRON ATOMS TO TOTAL NUMBER PRESENT

Catalyst	O_2 in gas, %	Final NH_3, %	Mg. of O_2 retd.	G.-atom of O	% of active Fe atoms of total	Ratio total atoms Fe to active Fe
918—pure iron	0.04	0.06	1.1	0.000069	0.04	2440
918—pure iron	.16	.03	1.6	.0001	.06	1680
921—iron + Al_2O_3	.04	.17	6.6	.00041	.25	404
921—iron + Al_2O_3	.08	.12	9.4	.00058	.36	280
921—iron + Al_2O_3	.16	.09	12.2	.00076	.46	218
921—iron + Al_2O_3	.24	.06	14.5	.00091	.55	183

Probably the best basis for the comparison of the two catalysts is that of some low and equal ammonia concentration. Thus, 918 on 0.04% of oxygen has its activity at 5000 space velocity reduced to 0.06% of ammonia, while 0.24% of oxygen is necessary to reduce the activity of 921 to 0.06% of ammonia. The oxygen retained is 1.1 mg. and 14.5 mg. which corresponds to about one active atom in 2000 for the pure iron and about one in 200 for the promoted catalyst. While it must be admitted that these are very approximate results, it is believed that the order of magnitude of the ratios is not far wrong.

That these unsaturated atoms are not all of equal activity is evident from the experimental results. Using those for Catalyst 921, given in Table I, and taking 5 mg. of oxygen as the quantity required to satisfy the lag, we see that the next additional 1.6 mg. of oxygen (0.04% of oxygen in gas) reduced the activity from 0.23 to 0.17% of ammonia. The next 2.8 mg. lowered it from 0.17 to 0.12% of ammonia, the next 2.8 mg. from 0.12 to 0.09% and the last 2.3 mg. from 0.09 to 0.06%. This is even more apparent from the results at 25,000 space velocity, where the first 5.5 mg. of oxygen lowered the ammonia concentration from 0.22 to 0.06%, while the next 6.5 mg. lowered it only an additional 0.03%. The other catalysts showed a similar behavior, thus indicating that the atoms of greater unsaturation, that is, those capable of being oxidized by the lower concentration of water vapor, account for the greater part of the ammonia synthesis.

The influence of promoters of the type alumina and potassium aluminate in increasing the number of unsaturated or active atoms may be illustrated in Fig. 1, which shows in a rough, qualitative way what the distribution of active atoms may be in the two cases. When catalysts of these two types are exposed to like concentrations of oxygen or water vapor in the gas phase, a steady state is realized, at which all atoms above a certain limiting degree of unsaturation are oxidized, and thus rendered inactive for ammonia formation. For a given concentration of oxygen, this state is represented by the line *a-a*. The effect of lower concentrations of oxygen would be represented by a line above *a-a*. We should expect, therefore, in accordance with the observed results, that a larger quantity of oxygen would be retained by the promoted catalyst by virtue of the greater number of atoms capable of oxidation; also, as was observed experimentally, that the amount of ammonia formed by the catalysts in this poisoned state would be greater for the promoted catalyst by virtue of its greater number of unsaturated atoms of lower activity (those below *a-a*) which were not oxidizable by the concentration of oxygen used.

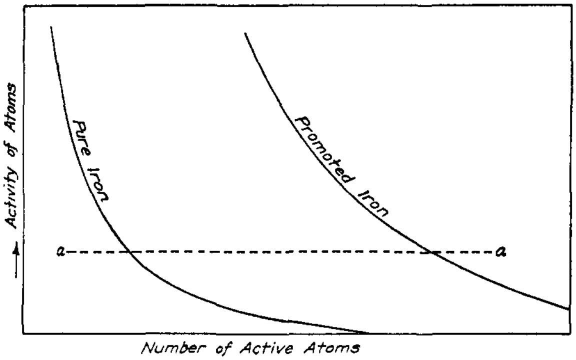

Fig. 1.—Relative distribution of active atoms in pure iron and promoted iron catalysts.

Some of the points of unsaturation are no doubt due to a distorted arrangement of iron atoms, brought about by reduction, in which their position relative to one another corresponds to some structure between that of the oxide and the iron crystal lattice. We know from the x-ray examination[12] of reduced metal catalysts that only the lines of crystalline iron

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[12] Ref. 8. p. 2872.

appear on the photographs. This means that most of the iron atoms of the oxide are rearranged to form the iron lattice during reduction, but it does not rule out the possibility of having a small part of the total iron present in distorted arrangements representing incomplete transition from the oxide to the iron crystal structure. The ability of the promoter to increase the number of such unsaturated atoms is probably due to its being so intimately associated in the magnetite lattice as to hinder the complete rearrangement to the iron lattice during reduction. Also, as was pointed out previously,[13] the presence of the promoter in the oxide favors the formation and maintenance of small iron crystals, thus providing a larger number of active atoms of the degree of unsaturation exhibited by surface atoms of the metal crystal lattice.

The upper limit of unsaturation to be found in these catalysts is not known, but the previous calculation made from the water-vapor—hydrogen ratio capable of causing oxidation indicated that the maximum average energy of a range of these active atoms responsible for a large part of the synthesis was about 12,000 cal. per gram atom above that of normal iron. Since the heat of vaporization of iron is probably at least 60,000 cal. per gram atom, it does not appear likely that there are present in reduced catalysts any appreciable number of atoms that possess a degree of unsaturation near that of the gaseous metal.

Summary

The inhibiting effect of small concentrations of oxygen or water vapor upon iron catalysts for ammonia synthesis, together with the accompanying oxide formation, is interpreted in terms of the concept which postulates the presence in the catalyst of active iron atoms of various degrees of unsaturation. Evidence is presented to show that both the catalytic activity for ammonia synthesis and the ability to form oxide in the presence of low concentrations of water vapor are properties of iron atoms in the same range of unsaturation. This permits an estimation of the number of active atoms from the amount of oxygen retained. The ratio of active atoms to the total iron in the catalyst is estimated at about one atom in two thousand for the pure iron and about one in two hundred for the promoted iron. The results show that the predominant effect of promoters of the type alumina and potassium aluminate is to increase the number of catalytically active atoms relative to the total number of metal atoms present.

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[13] Ref. 8, p. 2874.