5. Table VIII summarizes the results of duplicate hydrations on each solution. The values were obtained from a smooth curve representing the most probable curve for the two hydrations in each case.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE POISONING ACTION OF OXYGEN ON IRON CATALYSTS FOR AMMONIA SYNTHESIS

BY J. A. ALMQUIST AND C. A. BLACK

RECEIVED AUGUST 11, 1926 PUBLISHED NOVEMBER 5, 1926

Heterogeneous catalytic gas reactions in general are characterized by a marked sensitivity to inhibition or poisoning by the presence in the reacting gases of small concentrations of certain foreign substances. The substances that are known to act as catalyst poisons are many and the effect of each has been found to be dependent upon the type of catalyst that is being employed. It has been noted previously[1,2] that oxygen compounds are poisons for iron ammonia catalysts and that the inhibiting effect of small concentrations of several different oxygen compounds is proportional to their oxygen content. The present investigation was undertaken with the view of studying in a quantitative way the mechanism of the poisoning action of oxygen with particular regard to its effect on iron catalysts containing various promoters.

Experimental Part

The experiments were made at atmospheric pressure in a glass apparatus arranged as in Fig. 1. The catalysts used were of the series whose composition, preparation and activity at 100 atmospheres' pressure are described in connection with another investigation.[3]

Approximately 5 cc. of the catalyst to be studied was placed in the tube, 6, in the form of 10–14 mesh granules of the oxide. The weight of the oxidized catalyst used in each case was 12.95 ± 0.02 g. The tube was then sealed into place and heated to 444° by means of a boiling sulfur-vapor bath. Reduction was then begun by passing through a gas mixture of three parts of hydrogen to one of nitrogen. This gas was expanded from the high-pressure system, where it had undergone purification by passage over heated copper and nickel catalysts, soda lime and alumina gel. In order to insure a high degree of gas purity for these tests, the expanded gas was passed in order through Tube 1 containing platinized asbestos at about 300°, drying tubes containing soda lime and fused potas-

---

[1] Larson and Tour, *Chem. Met. Eng.*, **26**, 647 (1922).

[2] Almquist and Dodge, *ibid.*, **33**, 89 (1926).

[3] Almquist and Crittenden, *Ind. Eng. Chem.*, to be published later.

sium oxide, a capillary flowmeter and a coil immersed in liquid air before reaching the catalyst. Reduction was continued with a gas flow corresponding to 5000 space velocity, until the amount of water leaving the catalyst, as determined by absorption in the weighing tube, 7, containing fused potassium hydroxide, was less than 0.5 mg. per hour.[4] The catalyst has by this time attained a constant state of activity for pure gas as measured by the constant concentration of ammonia in the effluent gas. Free oxygen for the poison tests was provided by the electrolytic cell, 2, containing barium hydroxide solution, at the desired rate by controlling the current input furnished by a storage battery and measured by a milliammeter. When it was desired to change from pure gas to gas containing a definite concentration of oxygen, the incoming hydrogen-nitrogen gas was by-passed so as to take up the products of the electrolytic decomposition. Before beginning a run, this gas was allowed to pass into the atmosphere at Stopcock 5 for 15 minutes, in order to flush out the system thoroughly up to this point. The oxygen-containing gas was then passed over the catalyst. The oxygen output of the cell was checked at intervals by passing the gas over platinized asbestos and weighing the water formed.

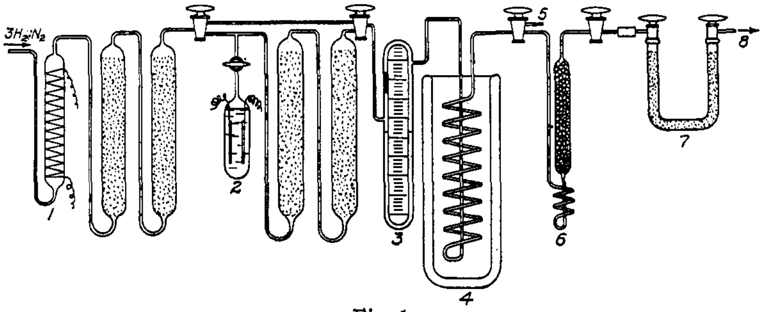

Fig. 1.

The moisture in the gases leaving the catalyst was collected in weighed tubes containing fused potassium hydroxide. The ammonia content was determined at frequent intervals by the usual method of absorbing the ammonia from a definite volume of the hydrogen-nitrogen mixture in water, titrating the sample to the end-point with the 0.01 *N* sulfuric acid using sodium alizarin sulfonate as indicator. Tests were also made for free oxygen in the dried exit gases by passage over platinized asbestos and through a weighed tube containing fused potassium hydroxide, but it was found that there was no oxygen passing the catalyst as such under the conditions of our experiments. All of the effluent gas during a run was passed through tubes of fused potassium hydroxide, and weighings of the moisture

---

[4] Fused potassium hydroxide is a satisfactory absorbent for low concentrations of water vapor in the presence of ammonia, for it does not take up ammonia unless it be used to the point where its surface becomes wet.

thus absorbed were made at the following stages of the poisoning process: (1) catalytic activity begins to decline; (2) activity shows no further decline; (3) two intervals after catalyst reaches lowest activity. At the conclusion of this treatment, the oxygen was shut off and pure gas again passed through. The moisture obtained during the reduction period was usually weighed at the end of one or two half-hour intervals and after the reduction had been continued overnight.

Results

The composition of the catalysts used and their activity at 1 atmosphere and 444° are given in Table I. Under these conditions, the equilibrium concentration of ammonia is about 0.23%. It is interesting to note that the alumina-promoted catalyst is somewhat more active at atmospheric pressure than is the one containing potassium oxide plus alumina, while tests at 100 atm. on the same catalysts have shown the marked superiority at higher pressures of the composite-promoted catalyst.[3]

TABLE I

ACTIVITY ON PURE GAS

Catalyst No.	Promoter content	% of NH_3 at space velocities of			
		5000	10,000	25,000	50,000
918	None	eq.	0.195	...	...
920	0.20% K_2O	0.211	.125	...	...
921	1.31% Al_2O_3	eq.	eq.	0.218	0.195
922	0.25% K_2O + 1.05% Al_2O_3	eq.	eq.	.215	.192

It is seen that the promoted catalysts 921 and 922 are capable of effecting about the same conversion at 25,000 space velocities as that of a pure iron catalyst at 5000 S. V. In order of decreasing activity under these conditions, the catalysts are 921, 922, 918, 920.

The effect of definite concentrations of oxygen on the activity of these catalysts at 5000 space velocity is given in Figs. 2 and 3. In these curves the percentage of ammonia is plotted against the time beginning with the admission of oxygen. At this rate of flow, S. V. 5000, all of the catalysts except 920 are capable of giving the equilibrium concentration of ammonia in pure gas, as represented by the concentration of ammonia at the beginning of the run. For the better catalysts, there is a marked interval of time or lag following the admission of the oxygen before any drop in the ammonia concentration occurs. For a given catalyst, the duration of this lag is inversely proportional to the concentration of oxygen. In all cases the drop in ammonia concentration, once begun, is rapid to a lower level, where the activity remains practically constant. Following the substitution of pure gas for that containing oxygen, the ammonia concentration rises again to the original value. For a given catalyst, the poisoning effect, as measured by the concentration of ammonia obtained after the drop to a steady value, varies with the concentration of oxygen.

Inspection of Fig. 2 and Fig. 3 shows for each catalyst that a four-fold increase in the oxygen concentration (0.04 to 0.16%) lowers the ammonia concentration by about one-half. That is, within this range, the amount of ammonia produced is inversely proportional to the square root of the

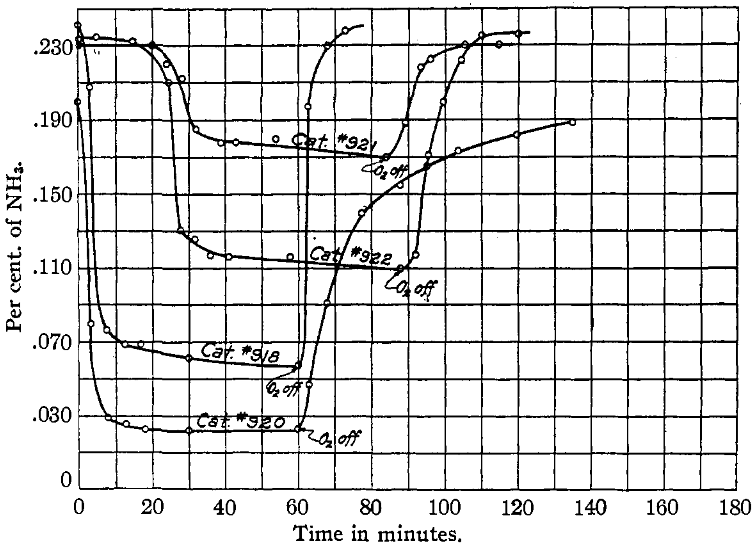

Fig. 2.—Effect of 0.04% O_2 by volume on the performance of various catalysts at S. V. 5000 and 444°.

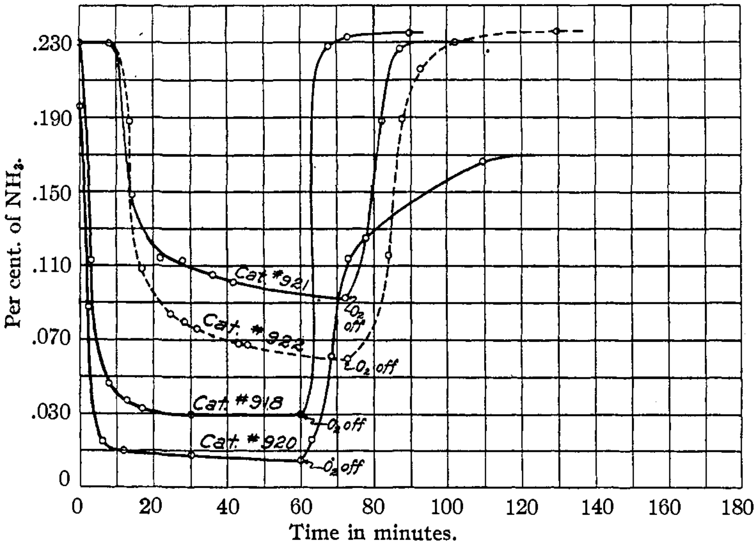

Fig. 3.—Effect of 0.16% O_2 by volume on the performance of various catalysts at S. V. 5000 and 444°.

oxygen concentration in the gas. The effect of various concentrations of oxygen on a promoted catalyst is represented by Fig. 4.

With equal concentrations of oxygen, it is seen that the order of activity of the catalysts on oxygen-containing gas is the same as on pure gas. The better catalysts are characterized by a longer lag than the less active, and the final steady ammonia concentration is considerably higher than for the latter.

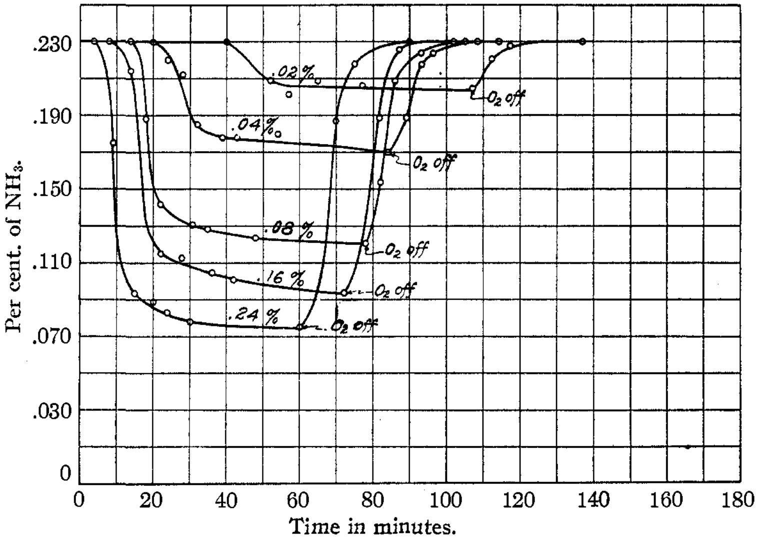

Fig. 4.—Effect of various concentrations of oxygen on the performance of Catalyst 921, a typical active promoted catalyst.

The determination of water in the gases leaving the catalyst showed that none was passed through during the period of lag; during the rapid drop in ammonia concentration, water was obtained but always in less amounts than corresponded to the oxygen input of the same period. After the ammonia concentration had leveled off at a nearly steady value, it was found that water was leaving the catalyst in quantities equivalent to the oxygen entering. The excess of oxygen introduced throughout the run over that appearing as water in the exit gases, therefore, represents that retained by the catalyst. The oxide thus formed is reducible by the pure gas mixture, and the determination of the water obtained during the reduction was in fair agreement with this excess of input oxygen.

The equivalence of oxygen in the entering and effluent gases during the last period of the run shows that a steady state with regard to oxide formation has been attained. The amount of oxygen retained by the catalyst is thus independent of the length of the run after this state has been reached. In Table II are given the results of the oxygen determinations for the various catalysts after treatment with gas containing definite concentrations of oxygen.

TABLE II

OXYGEN RETAINED AS OXIDE BY THE CATALYST

Catalyst	O_2 input, mg./min.	Concn. of O_2 in gas vol., %	Duration of run, min.	O_2 input, mg.	O_2 in exit, mg.	O_2 retained, mg.
918	0.25	0.04	60	15.0	13.9	1.1
	1.00	.16	60	60.0	58.4	1.6
920	0.25	.04	60	15.0	14.5	0.5
	1.00	.16	60	60.0	58.8	1.2
921	0.125	.02	107	13.4	8.6	4.8
	.25	.04	84	21.0	14.4	6.6
	.50	.08	78	39.0	29.6	9.4
	1.00	.16	76	76.0	63.8	12.2
	1.50	.24	60	90.0	75.5	14.5
922	0.25	.04	88	22.0	15.9	6.1
	1.00	.16	74	74.0	63.3	10.7

Several experiments were made on these same catalysts with gas containing water vapor. This was accomplished by introducing free oxygen and converting it to water prior to its admission to the ammonia catalyst by passage over heated platinized asbestos. The ammonia-concentration–time curves obtained on these runs were identical with those for the corresponding equivalent concentrations of free oxygen. The quantity of oxide retained by the catalyst was also the same, indicating that the same steady state is reached as in the case of free oxygen and that this virtual equilibrium which is established is concerned with the constituents iron—iron-oxide, water-vapor—hydrogen. The identical poisoning action of oxygen and water vapor bears out in a quantitative way results that have been obtained previously in the case of carbon monoxide and other oxygen compounds, namely, that the poisoning action of oxygen compounds is proportional to the oxygen content in those cases in which the oxygen is transformed into water under the conditions of the reaction.

The larger quantities of oxygen retained by the active promoted catalysts may suggest that this increase is due to the oxidation of aluminum resulting from the partial reduction of aluminum oxide by the treatment with pure gas. We have no evidence, however, that any reduction of aluminum oxide is possible under such conditions, but if it should occur, we know that it must be at an extremely slow rate. Therefore, if any of the oxygen retained by the catalyst during the poisoning period is held as the oxide of aluminum, it would not be reduced by pure gas so readily and quickly as is experimentally found to be the case with the oxygen that is actually retained. It must be concluded, therefore, that the oxygen in each case is retained as an oxide of iron and that the more active promoted catalysts are capable of forming larger quantities of oxide than the less active catalysts when exposed to like concentrations of oxygen or water vapor.

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.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE NATURE OF THE CATALYST SURFACE AND THE EFFECT OF PROMOTERS

BY J. A. ALMQUIST

RECEIVED AUGUST 11, 1926 PUBLISHED NOVEMBER 5, 1926

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).