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THE CATALYTIC SYNTHESIS OF WATER VAPOR IN CONTACT WITH METALLIC NICKEL[1]

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Introduction

When the oxidation of a metal and the reduction of the resulting oxide take place at temperatures not far removed from that at which the metal begins to promote the union of hydrogen and oxygen, the possibility exists that the catalysis proceeds by a mechanism of successive oxidation and reduction. Pease and Taylor[3] have shown that this hypothesis is consistent with all their results on the hydrogen-oxygen catalysis by metallic copper. With nickel, however, the claim is made that this mechanism is incapable of accounting for the observed facts, because nickel induces the combination of hydrogen and oxygen at temperatures considerably below that at which the reduction of nickel oxide begins.

Evidently the first question that must be decided is whether it is the hydrogen or the oxygen which is activated. The experiments of Bone and Wheeler[4] showed that the rate of combination of hydrogen and oxygen in contact with metallic nickel is nearly proportional to the partial pressure of the hydrogen and independent of the partial pressure of the oxygen. This result they explained on the assumption that the mechanism of the catalysis consisted in the adsorption and consequent activation of the hydrogen by the nickel. Subsequent work by various authors[5] has shown, however, that over the range in question the adsorption of hydrogen by nickel is independent of the pressure of the gas. Consequently, if the water formation really were due to impacts between gaseous oxygen molecules and adsorbed hydrogen, the reaction rate should be a function of the partial pressure of the oxygen, but independent of the hydrogen pressure. The relations observed by Bone and Wheeler seem to us, therefore, very strong evidence for the view that activation of the oxygen rather than of the hydrogen is the dominant factor in this catalytic reaction.[6]

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[2] National Research Fellow in Chemistry during the period covered by this investigation.

[3] Pease and Taylor, THIS JOURNAL, **44**, 1637 (1922).

[4] Bone and Wheeler, *Phil. Trans.*, **206A**, 1 (1906).

[5] Taylor and Burns, THIS JOURNAL, **43**, 1273 (1921). Gauger and Taylor, *ibid.*, **45**, 920 (1923).

[6] Similar objections may be raised to the conclusions of Bone and Wheeler in the case of all the catalysts studied in the research above mentioned. Even when, as in most cases, the adsorption isotherms are unknown, the fact that the reaction rate is

This activation of the oxygen might be due to adsorption or to the formation of a definite oxide of nickel, presumably nickelous oxide. If the latter mechanism is the correct one, the rate of water formation in the catalysis must be equal to the rate at which hydrogen reduces nickel oxide, when measured under comparable conditions. Our previous measurements[7] on the rate of reduction of nickel oxide by hydrogen showed this to be an interfacial reaction, that is, a reaction whose rate depends on the area of contact between the two solid phases, nickel oxide and nickel. Starting with pure nickel oxide the initial rate is zero, but after a certain lapse of time, which is longer at lower temperatures, reduction begins and accelerates autocatalytically. Obviously, therefore, the rate of reduction of nickel oxide can be expected to equal the rate of combination of hydrogen and oxygen only when the interface area between the nickel oxide and the nickel is the same in both cases. It was also shown that the rate of reduction of nickel oxide is less the higher the temperature to which it has been heated prior to reduction. Hence comparison of the rates of reduction and catalysis is further restricted by the requirement that the oxide to be reduced must not have been heated to a temperature higher than that used in the catalysis.[8]

The present experiments on the combination of hydrogen and oxygen in contact with metallic nickel were undertaken with the purpose of securing data to test the oxidation-reduction hypothesis. In particular, we wished to find whether oxide is really formed under the conditions of the catalysis, and if so, whether hydrogen will reduce this oxide at a rate sufficient to account for the catalysis.

Since this investigation was completed, a paper has been published by Larson and Smith[9] on the same subject. Although there are significant minor differences between the two sets of experiments, probably due to the differences in procedure, the point we wish to emphasize here is the qualitative agreement obtained. The brief account of our experimental results presented below is, therefore, offered mainly in confirmation of the experiments of Larson and Smith. In the discussion of their results, however, these authors have not realized that the reduction of nickel oxide by hydrogen is an autocatalytic process, and hence they conclude, in agreement with Bone and Wheeler, that reduction of the "stable" oxide is not an important part of the catalytic mechanism. On the other hand, it is

independent of the oxygen pressure is alone sufficient to show that the reaction mechanism cannot be simply that of gaseous oxygen striking adsorbed hydrogen.

[7] Benton and Emmett, THIS JOURNAL, **46**, 2728 (1924).

[8] Since Bone and Wheeler (Ref. 4) did not take either of these factors into consideration, their claim to have disproved the oxidation-reduction mechanism for the hydrogen-oxygen reaction cannot be accepted in the case of the base metal or metallic oxide catalysts.

[9] Larson and Smith, THIS JOURNAL, **47**, 346 (1925).

the main purpose of the present paper to show that a consideration of the reduction kinetics of nickelous oxide leads to the conclusion that the catalytic formation of water is due largely, and perhaps wholly, to reduction of this oxide.

Experimental Method

The apparatus and experimental procedure were the same as those employed in the previous work on the reduction of nickel and iron oxides.[7] The method, which is essentially that used by Pease and Taylor[8] in their study of the hydrogen-oxygen catalysis by metallic copper, was briefly as follows.

A constant current of pure dry hydrogen was passed through the catalyst, which was supported in the inner tube of a double-walled electric furnace. Oxygen was added to the hydrogen in any desired proportion by electrolyzing barium hydroxide solution at a suitable rate and admitting into the hydrogen line the electrolytic gas thus produced. The rate of reaction was determined at frequent intervals by absorbing and weighing in a calcium chloride tube the water formed during (usually) five minutes' passage of the exit gases from the furnace. Particular care was taken to prevent condensation of the water before reaching the calcium chloride tube. To insure reliable results it was found necessary to have the bulb of the thermometer used in measuring the reaction temperature extend well into the catalyst mass and also to avoid the use of rubber connections in the heated zone.

The hydrogen current was maintained constant throughout each experiment at 50 cc. per minute (0°, 760 mm.). Since the hydrogen was always in excess, it is convenient to express the oxygen concentrations in terms of the number of milligrams of water which would be formed if all the oxygen passing through the catalyst during a five-minute period were converted to water. For this purpose we will employ the expression, "oxygen equivalent to X mg. of water (per five-minute interval)." The corresponding volume concentrations are 2.45% when X equals 10 and 4.77% when X equals 20. The rate of the reaction is expressed as the number of milligrams of water actually obtained per five-minute interval

The same sample of catalyst was used in all the experiments. It was obtained by reduction with hydrogen at 400° of a sample of strongly ignited nickel oxide. The sample was held in the tube by a plug of glass wool and reduction carried out *in situ*. The loose catalyst mass thus formed was cylindrical in shape, 2.1 cm. in diameter and approximately 2.5 cm. high, and weighed about 15 g.

Experimental Results

Preliminary runs were made at different temperatures with a concentration of oxygen equivalent to 10 mg. of water per five-minute interval. At

100° and at higher temperatures the oxygen was converted quantitatively into water, with little or no permanent oxidation of the surface. At 35° the conversion to water was nearly zero, although large quantities of oxide were formed. The results obtained at two intermediate temperatures, 65° and 82°, are shown in Curves 5 and 6, Fig. 1.

The general features of the 65° run are typical, and will be discussed in detail. The rate of water formation rose gradually to about 50% conversion at the end of 80 minutes and then quickly decreased to about 5%. Here the oxygen was cut off and hydrogen alone passed over the catalyst at the same temperature, with the result that the water yield at once decreased to an immeasurably small value. After some time oxygen equivalent to 10 mg. of water per five-minute interval was again introduced with the hydrogen. As Curve 5 shows, the rate of water formation rose temporarily nearly to 20% conversion, but soon fell off to a small value. At this point the oxygen was again cut off, the temperature was raised to 108° and hydrogen alone passed over the catalyst. In four hours 83 mg. of water was obtained; at the end of this time reduction was still taking place, but at a very slow rate. If we make the reasonable assumption that this 83 mg. of water was produced by reduction of oxide, it follows that in this run nickel oxide was actually formed during the progress of the catalysis. It is natural to infer, then, that the sudden decrease in the rate of catalysis which occurred 80 minutes after the start of the run was due to complete oxidation of the surface of the nickel. That the conversion decreased only to 5%, rather than to zero, would indicate that nickel oxide itself possesses considerable catalytic activity in the hydrogen-

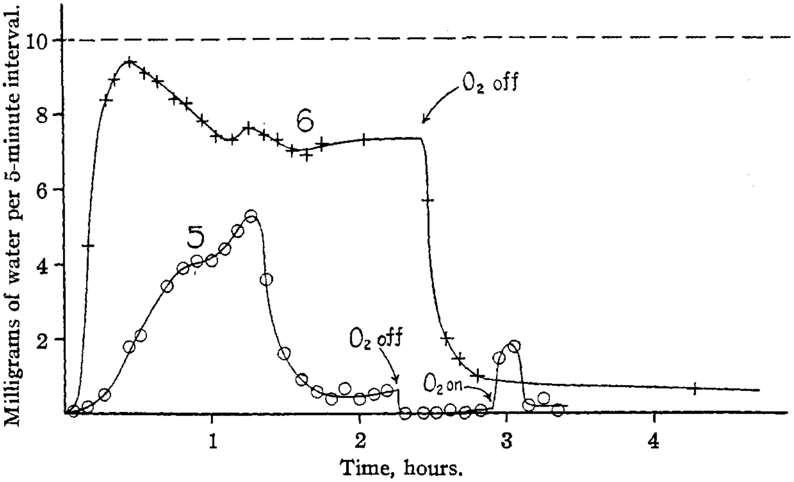

Fig. 1.—Oxygen concentration equivalent to 10 mg. of water per five-minute interval. Curve 5, Run 5 at 65°; Curve 6, Run 6 at 82°.

oxygen reaction—a fact which we had previously observed.[7] When the oxygen was cut off with the surface in the completely oxidized condition, hardly a trace of reduction occurred, doubtless because the surface did not contain the nickel nuclei which are necessary for the progress of this autocatalytic reduction. That a very slight reduction did finally occur, however, is shown by the fact that on subsequently readmitting the oxygen-hydrogen mixture, water was produced for a short time at a rate three or four times as great as that obtained with the completely oxidized surface; but the oxygen quickly healed the break caused by this slight reduction and the rate of catalysis once more fell off nearly to zero.

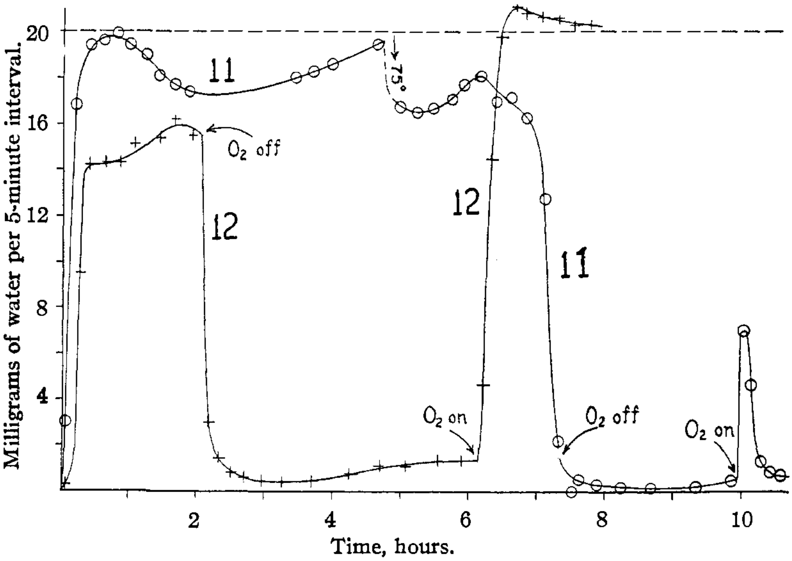

Fig. 2.—Oxygen concentration equivalent to 20 mg. of water per five-minute interval. Curve 11, 85° at start, later lowered to 75°; Curve 12, 75°.

These preliminary runs indicated the uselessness of attempting to determine the kinetics of the reaction at low temperatures, since they show that no steady state is reached except when the conversion is either very small or practically complete. For this reason we confined our further efforts to comparing rates of catalysis with rates of reduction.

At this point the catalyst was activated somewhat by several alternate oxidations and reductions, followed by a five-hour period at 350° in a current of hydrogen. With the catalyst in this form a series of experiments was made (Runs 10 to 14), using an oxygen concentration equivalent to 20 mg. of water per five-minute interval. The results[10] will be clear from Figs. 2 and 3, where the experiments are numbered in the order in which

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[10] Run 10 is omitted from the figures, as the curve is essentially similar to that of Run 14.

they were performed. It should be added that at the conclusion of Run 11, the oxidized surface was completely reduced by hydrogen at 154°; 167 mg. of water was thus produced. Reduction of the partially oxidized surface remaining at the end of Run 14 yielded approximately 40 mg.

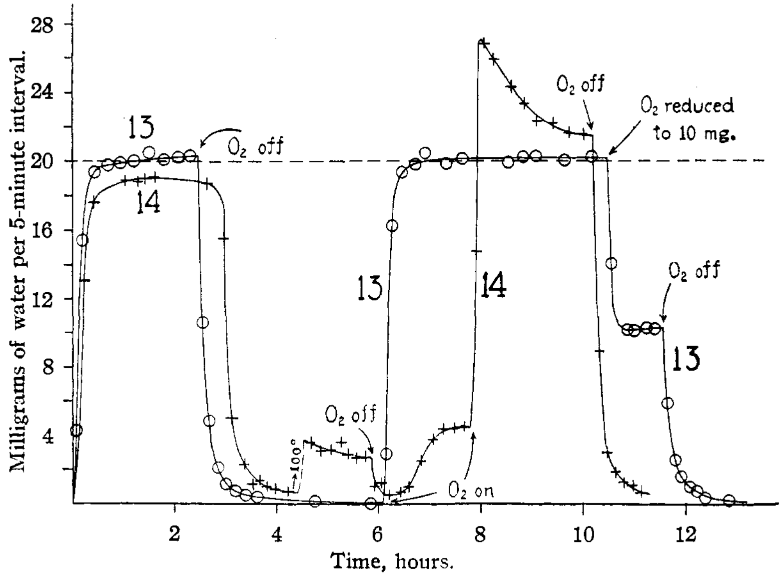

Fig. 3.—Oxygen concentration equivalent to 20 mg. of water per five-minute interval. Curve 13, 75°; Curve 14, 67° at start, later increased to 100°.

Discussion

Since in most of these experiments large quantities of water were obtained after shutting off the oxygen, it is evident that during the catalysis oxygen was permanently fixed in some form by the catalyst. There can be little doubt that this oxygen was present as a relatively thick layer of nickel oxide rather than as a monomolecular film of adsorbed oxygen. This conclusion is based mainly on the fact that the amount of oxygen necessary to "poison" the surface completely was equivalent to 167 mg. of water in Run 11, and to 188 mg. in Run 14, or about 180 mg. on the average; this is equivalent to 7.5 cc. of oxygen per gram of nickel, whereas the maximum adsorption observed by Taylor and Burns[5] for a sample similarly prepared was 0.5 cc. per gram, in the case of hydrogen, and still less for other gases. As a further argument in favor of oxide it may be noted that the reductions showed the autocatalysis which is characteristic of nickel oxide.

The failure to reach a steady state at efficiencies below 100% may be attributed to this progressive formation of nickel oxide. So much oxide is finally formed that the catalyst loses its activity almost entirely. If none of this oxide is reduced during the catalysis, obviously none of the water is formed through a mechanism of successive oxidation and reduction involving nickel oxide. In this case the catalysis would presumably be due to reaction between gaseous hydrogen and adsorbed oxygen, accompanied by a side reaction—formation of nickel oxide—which gradually poisons the catalyst. If, on the other hand, any of the nickel oxide is reduced during the catalysis, then to this extent successive oxidation and reduction must be a part of the catalytic mechanism. In the limiting case in which this is the sole mechanism, the formation of nickel oxide must favor catalysis as long as the interface area between the oxide and the metal increases; but when the surface is entirely oxidized, the interface area and, consequently, the rate of reduction, fall to zero. Therefore, although a number of minor points might be raised which seem to favor the oxidation-reduction mechanism,[11] the most direct evidence is to be found in the comparison of the actual rates of reduction and catalysis.

The highest rate of reduction observed at 75° (Curve 12, Fig. 2) was 1.3 mg. of water per five-minute interval; at 100° the maximum rate was 3.0 mg. in Run 10, and 4.5 mg. in Run 14 (in which the catalyst was considerably more active than in Run 10). Even with the relatively inactive catalyst of Run 5 some reduction occurred at 65° and the rate would doubtless have considerably increased had the run been continued. These results show that even at the lowest temperatures used in the catalysis, reduction takes place at an appreciable rate as long as the surface is not completely covered with oxide. But they also show that unless the rate of reduction *in the catalytic process* is much greater than the rates here observed, successive oxidation and reduction can have only a minor share in the catalytic mechanism.

It may be noted that somewhat higher rates of reduction were observed when oxygen was admitted with the hydrogen.[12] Thus in the latter half of Run 14, when oxygen equivalent to 20 mg. of water per five-minute interval was introduced, the rate of water formation rose temporarily to 26.8 mg. per five minutes; of this yield not less than 6.8 mg. must have come from reduction of oxide, although the final reduction rate before turning on the oxygen was only 4.5 mg. In Run 10 a corresponding increase from 2.3 to 5.5 mg. was observed. Striking as these increases are, they are nevertheless far from sufficient to make the rate of reduction comparable with that of the catalysis.

[11] Interpretation of the shape of the curves obtained and other similar details is rendered difficult by the fact that, in any given run, the zone of reaction apparently moves gradually through the sample from top to bottom.

[12] Since the temperature was ordinarily constant within ±0.5° and the thermometer bulb was imbedded in the catalyst, there seems to be no possibility that these increases are due to a general rise of temperature throughout the catalyst. A purely local temperature rise resulting from the combination of hydrogen and oxygen is, however, not improbable.

On the other hand, since there is no reason to suppose that the interfacial area between the oxide and the nickel was of the same order of magnitude in the reductions as in the catalytic experiments, it was not to be expected that the two rates would be equal. In heterogeneous reactions of this type the extent of interface evidently depends not only on the extent to which reaction has proceeded, but also on the number of centers at which it began. Our previous results on the reduction of pure nickel oxide at low temperatures suggest that the reaction began at but few points and spread more or less spherically from these as centers. Since the reduction curves obtained in the present investigation are closely similar in form, it seems justifiable to conclude that here also reaction starts at only a few centers. Under these conditions the area of the interface between the two solid phases will always be very small in comparison with the area that would be present if the reaction began at many points distributed over the whole surface of the catalyst.

This raises the question whether the oxidation of the nickel actually occurs in such a way as to produce a relatively large area of contact between the two solid phases. Evidently the first oxygen molecules which strike the metal surface and form oxide must be in a very active state, since they are surrounded on all sides by free nickel atoms. Nevertheless, if the oxidation of a completely reduced surface, like the reduction of a completely oxidized one, spread autocatalytically from only one or two centers, there would be no reason to believe that the area of the interface would be greater in the catalytic process than in the reduction of the completely oxidized surface with hydrogen alone. Since all available data show,[13] however, that oxidation begins practically simultaneously over all of the surface with which oxygen comes in contact, the conclusion follows that the interface area and, consequently, the rate of reduction must be very much greater in the catalysis than is indicated by the results of our reduction experiments. An 8- or 10-fold increase is all that is necessary to make the observed reduction rates equal to the rates of catalysis. The necessary increase appears to be still less in the experiments of Larson and Smith.[9,14] While it is impossible at present to prove that the water formed in the catalysis comes *exclusively* from reduction of nickel oxide, we believe that this interpretation is consistent with all of the facts now known.

[13] Although there are strong theoretical reasons for believing that the oxidation of a metal must take place more readily at the interface between the solid phases if the reduction (or dissociation) of the oxide is interfacial, the experiments of Tammann and Koster [*Z. anorg. Chem.*, **123**, 196 (1922)] and others show that the initial formation of oxide nuclei occurs at such a large number of centers that autocatalysis is not ordinarily observed in these cases.

[14] The two sets of experiments are not directly comparable since most of the experimental conditions, such as rate of flow, oxygen concentration, height of catalyst sample, etc., were different in the two cases.

In conclusion, we wish to record our indebtedness to the Carnegie Institution of Washington for financial aid in this investigation from a grant made to Professor A. A. Noyes.

Summary

1. A study has been made by a flow method of the combination of hydrogen and oxygen in contact with reduced nickel, using oxygen concentrations up to 5%.

2. At all temperatures at which any water formation could be detected it was found that superficial oxidation of the nickel readily took place. At the lower temperatures this oxidation eventually covered the whole surface, with the result that the rate of catalysis suddenly decreased to a small value.

3. When hydrogen was passed over a catalyst superficially oxidized in this way, the rate of reduction accelerated autocatalytically, in conformity with the previous observation that the reduction of ordinary nickel oxide is an interfacial reaction, that is, a reaction whose rate depends on the area of contact between the two solid phases. However, the maximum rates of reduction so obtained were always small in comparison with the rates of the hydrogen-oxygen catalysis at the same temperature.

4. Arguments are presented to show that the area of contact between the nickel oxide and the nickel and also, therefore, the rate of reduction, are very much greater in the catalytic process than in the reduction of a completely oxidized surface by hydrogen alone.

5. From a consideration of the work of Bone and Wheeler it is concluded that activation of the hydrogen does not play a prominent part in this catalytic reaction.

6. The conclusion is reached that the catalytic water formation can be largely and perhaps entirely accounted for on the hypothesis of successive oxidation and reduction of the catalyst.

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