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

THE SYNTHESIS OF WATER OVER NICKEL AND COPPER CATALYSTS

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RECEIVED OCTOBER 24, 1924 PUBLISHED FEBRUARY 5, 1925

The catalytic formation of water in the presence of certain noble metals, particularly platinum, has been the subject of investigation for many years. The acceleration produced by base metals, however, received little attention until 1906, when Bone and Wheeler[1] reported experiments that included nickel and copper. More recent investigators of such metals have largely confined their efforts to the study of copper. An extensive investigation of the catalytic action of this metal has been made by Pease and Taylor.[2] These experimenters confirmed the earlier observations of Bone and Wheeler,[1] and of Joannis,[3] that the metal surface was always oxidized during the catalysis. They also found that the oxide that was formed simultaneously with water was rapidly reduced by oxygen-free hydrogen and that water was formed thereby at a greater rate than by catalysis. Between 130° and 100° they observed a marked decrease in the catalytic activity of the copper, in the rate of reduction of the oxide, and in the rate of oxidation of the copper. Largely on the basis of these observations Pease and Taylor have assumed that catalysis takes place on copper mainly through the formation of an oxide and its subsequent reduction. These investigators have suggested, however, another explanation of the synthesis, namely, that activation of an oxygen molecule takes place as it is about to combine with the copper to form oxide, in which activated condition it is open to attack by the hydrogen. This mechanism was referred to as "incipient oxidation." It differs from the alternate oxidation and reduction mechanism only in the length of time the oxygen is attached to the copper. According to Pease and Taylor all the facts of this catalysis are explained by the alternate oxidation and reduction mechanism. As a consequence very little importance was attached to the "incipient oxidation" idea.

So far as the direct synthesis of water is concerned, little attention has been given to the catalytic properties of nickel. Pease and Taylor[2] state that nickel will catalyze this reaction even at room temperature, that it is slowly oxidized in the air at this temperature, that the oxide formed is not reducible below 100° to 150°, and that the oxidized material is inactive as a catalyst.[4] They conclude that "the chemical properties

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

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

[3] Joannis, *Compt. rend.*, **159**, 64 (1914).

[4] Similar observations have also been made by Rideal, *J. Chem. Soc.*, **121**, 309 (1922).

of the catalytic material are in no way related to its activity as a catalyst," and that "clearly, with nickel it is a case of purely contact action."

The experiments which have been made in this Laboratory indicate that there are no marked differences in the behaviors of nickel and copper when employed as catalysts in the direct synthesis of water. It is the purpose of this paper to present the experimental results of a direct comparison of the catalytic action of these two metals and to offer some suggestions as to the possible mechanisms involved.

Preparation of Catalytic Material

The nickel and the copper catalysts employed in the experiments reported in this paper were made by the reduction of the oxides. The preparation of the metallic catalyst therefore involved two steps: (1) the preparation of the oxide and (2) its reduction by hydrogen.

Preparation of the Oxide.—In the preparation of the oxide, the following procedure[5] was employed.

> A 6% solution of nickel (or copper) nitrate in distilled water was neutralized with ammonium hydroxide of like concentration, the temperature of the solutions being about 45°. After the precipitate had been washed three or four times with distilled water, it was filtered off under suction and then dried for a period of 24 hours at 75° to 80° and for an additional 24 hours at 120° to 130°. The resulting material was crushed and screened to 8–14 mesh. In preparing the oxides only chemically pure materials were employed. Since appreciable quantities of dissolved salts are carried down by the precipitate, it was important to employ distilled water throughout. To avoid any non-volatile substance other than the metallic oxide, ammonia was employed as a precipitant rather than one of the alkali metal hydroxides. Any ammonium or metal nitrate carried down by the precipitate was readily decomposed during the subsequent heat treatment of the oxide.

Reduction of the Oxide.—In studying the reduction of copper oxide by hydrogen at temperatures between 100° and 200° several investigators[6] have reported a characteristic incubation period during which no reduction takes place. Such an incubation period has not been observed when oxides of nickel are reduced.

Pease and Taylor[2] have concluded from their experiments that the reduction of copper oxide is auto-catalytic, the reduction taking place only at a copper-copper oxide interface. The incubation period, therefore, represents the time required to develop the necessary interface. Pease and Taylor found that this time was increased as the temperature of reduction was lowered and was indefinitely extended when the reducing gas contained

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[5] The essential features of this procedure were first suggested by Merrill and Scalione, THIS JOURNAL, **43**, 1982 (1921).

[6] Wright and Luff, *J. Chem. Soc.*, **33**, 1, 504 (1878). Wright, Luff and Rennie, *ibid.*, **35**, 475 (1879). Wright and Menke, *ibid.*, **37**, 785 (1880). Berger, *Compt. rend.*, **158**, 1798 (1914). Sabatier and Espil, *ibid.*, **158**, 668 (1914). Pease and Taylor, THIS JOURNAL, **43**, 2179 (1921). Palmer, *Proc. Roy. Soc.*, **103A**, 444 (1923).

a high concentration of water vapor. Since the exact conditions under which reduction is carried out are undoubtedly of importance in determining the performance of the copper catalyst, it seemed desirable to examine further this peculiar behavior of copper oxide before definitely fixing the conditions of reductions.

As a result of experiments made in this Laboratory on the reduction of copper oxide it was found that there was no incubation period even at a temperature as low as 106°, when the copper oxide and the hydrogen were free from water. In these experiments water was removed from the oxide by evacuation at 218°. Pure, dry, electrolytic oxygen was then passed through the oxide at this same temperature in order to insure complete oxidation of the copper. Any copper-copper oxide interface which might have developed during the evacuation was no doubt destroyed by this treatment. The catalyst was then cooled to room temperature and the oxygen displaced by pure, dry hydrogen. At 106° reduction began immediately. When the hydrogen was humidified at 0°, however, the reduction was delayed about one hour, while humidification at 20° produced an incubation period that lasted more than six hours. After reduction had started, it proceeded in a normal manner, the maximum rate being somewhat lower than with dry hydrogen. This same retardation was observed when water was added after reduction had begun. Thus, for example, with hydrogen humidified at 0° the retardation was found to be about one-fourth; with hydrogen humidified at 20° it was about one-half. As long as the water was present, the reduction rate remained fairly constant, showing no indication of rising again.

The study of the reduction of copper oxide which has just been referred to led to the adoption of a uniform procedure in the preparation of both the copper and nickel catalysts. In each case dry, electrolytic oxygen was passed through the oxide at a temperature of 218° until all the water was removed. The oxide was then cooled to room temperature and the oxygen displaced by dry hydrogen. The temperature was then raised to 106° at which temperature the reduction was continued for three to four hours. The temperature was gradually increased to 218° where the reduction was completed.

The oxides shrank by different amounts on reduction. Nickel decreased in volume by about one-tenth, while copper, in some cases, shrank as much as six-tenths. For this reason the volumes of reduced catalyst was not all the same. In some cases in which the shrinkage was known to be great, more than 10 cc. of the original material was taken in order to insure a sufficient amount of the reduced contact material. Generally, there was present after reduction between 7 and 9 cc. of catalyst. It is believed that this variation does not affect the validity of the results.

Experimental Part

The experimental procedure was essentially as follows. Hydrogen, containing definite amounts of oxygen, was passed over the reduced metal catalyst at a given temperature and the water formed was weighed after absorption in phosphorus pentoxide. The oxygen that escaped combination was determined by passing the dried, effluent gases over hot palladium-asbestos and weighing the water formed. The oxygen retained by the catalyst during the synthesis was determined by weighing the water obtained by reduction of the catalyst at the conclusion of the catalytic run. The detailed arrangement of the apparatus is shown in Fig. 1. With the exception of rubber connections for attaching the weighing tubes, the apparatus was built entirely of glass.

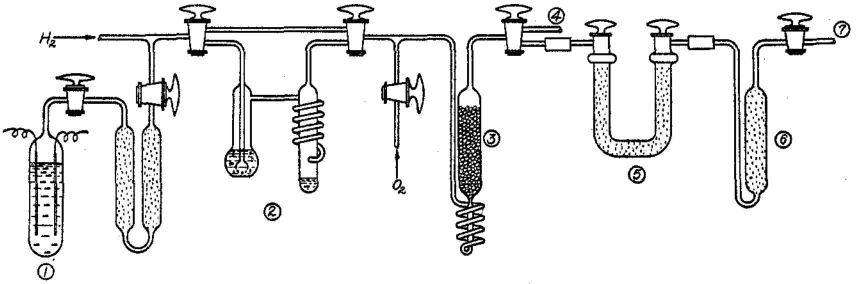

Fig. 1.

The hydrogen was prepared by electrolysis of a solution of sodium hydroxide, and purified by passing it first through a tube of reduced copper at 310°, where oxygen was converted to water and then through a tube of soda lime where water was removed as well as any carbon dioxide which might be present. To insure the complete removal of oxygen and water vapor the gas was finally passed through a tube of palladium-asbestos at 310° and two tubes of fused potassium hydroxide placed in series. The hydrogen was occasionally tested for condensable vapors by passing it through a bulb immersed in liquid air. No attempt was made to remove the small amounts of nitrogen which were present in the gases.[7] It was assumed that a trace of nitrogen had no appreciable effect on the reaction.

Oxygen was added to the hydrogen from an electrolytic cell as indicated in Fig. 1. The electrolytic gases were dried by passage over soda lime and fused potassium hydroxide. Barium hydroxide was used as electrolyte in order to avoid any possible contamination of the gases by carbonate decomposition. The concentration of the oxygen was measured in terms of equivalent milligrams of water per five-minute interval, a convenient standard adopted by Pease and Taylor[2] in their study of copper. The oxygen concentration was confirmed by passing the gases through a tube of hot palladium-asbestos and weighing the water formed. The deviations from the theoretical value for a period of 10 minutes were less than one part in 200 (using 10 mg. of O_2).

The rate of flow of the hydrogen was established at 100 cc. per min. (0°, 760 mm.)

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[7] Analyses of the electrolytic hydrogen showed less than 0.1% nitrogen present. This small amount was probably due to air that had diffused through the water seal of the hydrogen holders.

and was measured by means of a capillary flowmeter attached by a length of rubber tubing to the final phosphorus pentoxide weighing tubes. The flow was regulated before the addition of oxygen to the gas and was found to remain steady during the period of a run. It was checked at alternate weighings, that is, while the flow was through (7), at which point all of the oxygen had been converted to water by combining with the equivalent amount of hydrogen produced in the electrolytic cell (1). The small amount of hydrogen that was left in excess, due to combination of the equivalent amount of oxygen with the catalyst, did not cause an appreciable error in the rate of flow.

The gases, either hydrogen alone or hydrogen with added oxygen, were saturated with water vapor when desired by passing them through a humidifier (2). The humidifier was a water bubbler maintained at room temperature, followed by a condensing coil and tube immersed in a thermostat. By this arrangement the gases were saturated at a higher temperature than desired and the excess of moisture was subsequently removed by condensation. Saturation at 0° gave a water-vapor concentration of 0.6% by volume, while at 10° the concentration was 1.2% by volume. With a flow of hydrogen of 100 cc. per minute, these concentrations were equivalent to 2.44 mg. and 4.89 mg. of water per five-minute interval, respectively.

The tube (3) containing the catalyst was about 1 cm. in internal diameter. It was provided with a preheating coil which brought the gases to the temperature of the bath before they entered the catalyst chamber. Heating was effected by means of vapor-baths[8] which insured a uniform temperature throughout the catalyst mass.

A typical experiment was as follows. After sweeping out the system with pure hydrogen at room temperature, the catalyst was heated to 184° and weighings were made (at 4) to insure the absence of moisture in the gases leaving the catalyst. The maximum allowance of water was 0.1 mg. in 10 minutes (1 liter of gas). The vapor-bath surrounding the catalyst was then changed to give the desired temperature, the oxygen analytical train was connected and flushed and the palladium-asbestos tube (6) was brought to temperature. The effluent gases were again tested for moisture to make certain that the sweeping of the system had been complete. The desired concentration of oxygen from the electrolytic cell (1) was then added to the hydrogen. A run was considered to begin at this point. Weighings were made thereafter at five-minute intervals—alternately at (4), "synthesis," and at (7), "leakage"—except in a few special cases in which successive values for the synthesis at the beginning of the run were desired. These weighings, plotted against time, gave the rates of synthesis and oxygen leakage, respectively. At the conclusion of the catalytic run, the oxygen was shut off, the oxygen analytical train was disconnected and pure hydrogen was passed over the catalyst to reduce the oxide formed during the catalysis.

Experimental Results for Nickel

The experimental results for nickel are shown graphically in Figs. 2 and 3. Fig. 2 shows the behavior of nickel (temperature of the vapor-bath, 34°) when oxygen equivalent to 10 mg. of water per five-minute interval was admixed with the hydrogen. It will be noted that the water production increased rapidly to a maximum, remained constant for approximately two hours and then fell rapidly to zero. During the period of maximum activity the oxygen that escaped combination was practically nil; the oxygen leakage, however, rapidly increased as the water

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[8] The substances used were ethyl ether, 34°; ethyl alcohol, 78°; *iso*butyl alcohol, 106°; *iso*-amyl alcohol, 131°; aniline, 184°; and naphthalene, 218°.

formation decreased, soon reaching a point where all the oxygen introduced passed unchanged through the catalyst. When the flow of oxygen was interrupted and pure hydrogen was passed over the catalyst, water was again formed due to the reduction of the oxide developed during the synthesis. This reduction was found to be complete at 34° in the presence of pure hydrogen. The oxide together with the water formed catalytically and the oxygen leakage accounted for all the oxygen introduced. When oxygen was again added to the hydrogen, the phenomena already observed were reproduced.

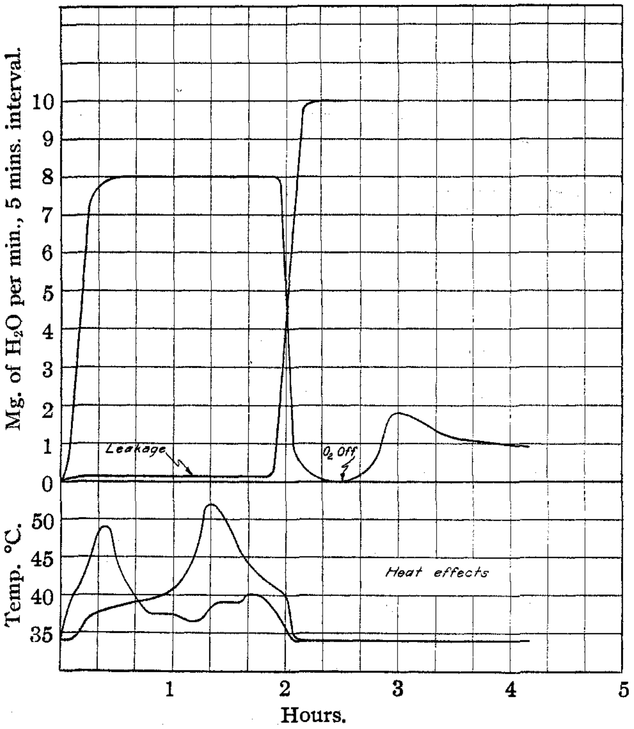

Fig. 2.

Although the oxide formed on the nickel during the synthesis was not visible, differing in this respect from results obtained with copper, its slow movement through the catalyst mass could be followed by the temperature effects produced as the synthesis proceeded. For this purpose thermocouple junctions were placed 2.5 and 7.5 cm. from the bottom of the catalyst bed, which had a total depth of 10 cm. The lower curves in Fig. 2 show the heat changes within the catalyst mass as measured by the thermocouples at these two levels. The curves for catalysis and for temperature are plotted on the same time axis so that comparison of catalytic and heat phenomena may be made directly. The curves for the heat effects indicate a moving heat zone that traverses the catalyst mass during the period of maximum catalytic action and reaches the upper end simultaneously with the drop in the rate of synthesis. A measured, maximum temperature of 52° was recorded during the experiment. The simultaneous drop of the synthesis and heat curves indicates that synthesis takes place in that portion of the catalyst which is coincident with, or just ahead of, the moving oxide boundary. This was probably to be expected, since the maximum temperature of the system lay within this region.

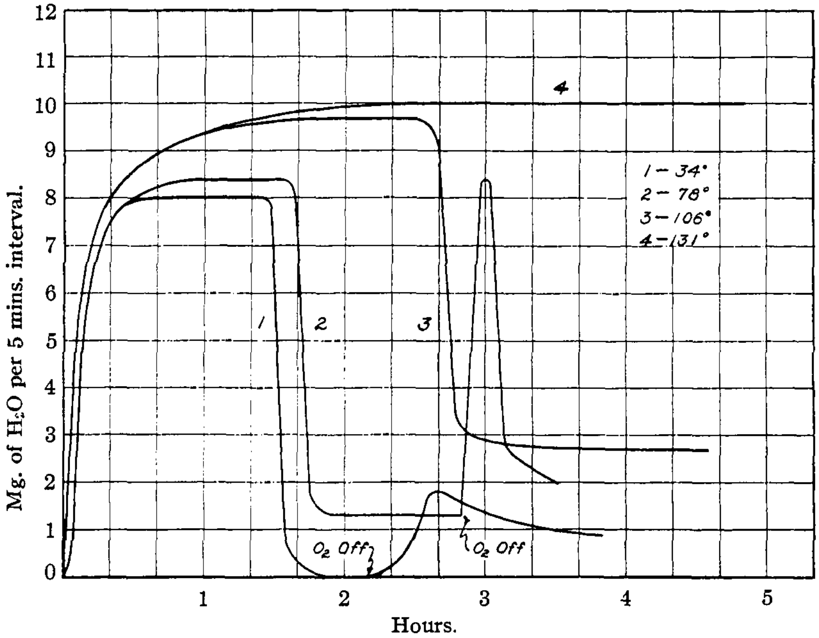

Fig. 3.

Fig. 3 shows the effect produced when the temperature of the catalyst was varied. As would be expected, the efficiency of the catalyst increased with rise in temperature and the period of maximum activity was lengthened. Moreover, at the higher temperatures, after the passage of the heat wave, the contact material continued to manifest some catalytic activity; at 131° the efficiency quickly rose to 100% and remained constant at that value.

Experimental Results for Copper

Unfortunately no direct comparison of nickel and copper could be made at 34° because the rate of catalysis on copper at this temperature was so slow as to preclude measurement. The experimental results obtained on copper at slightly higher temperatures are, however, strikingly similar to those for nickel. The curves in Fig. 4, which are in agreement with those obtained by Pease and Taylor,[2] show that copper also possesses initially a high activity. In the case of copper, however, the drop to the lower level was not so abrupt as with nickel. Furthermore, the difference between the high initial activity and the final steady state was not so great for copper as for nickel, particularly at the lowest temperature studied (78°). This difference is undoubtedly due to the lower activity of the copper as compared with that of the nickel.

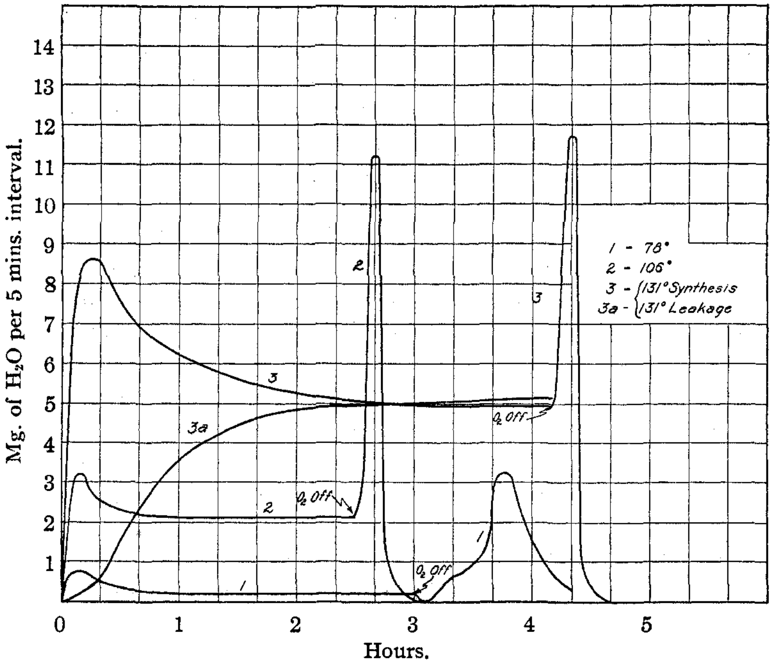

Fig. 4.

The oxide formed on copper during the synthesis is plainly visible and its movement through the catalyst mass can be easily observed. However, the oxide formation and its movement through the catalyst bed were not as sharply defined as was found to be the case with nickel. An examination of the temperature effects produced while the synthesis was in progress failed to disclose the progression of any sharply defined heat wave such as was observed with nickel. Since the heat of formation of copper oxide is less than half that of nickel oxide and the thermal conductivity of copper is about ten times that of nickel, the possibility of developing a region of high temperature would seem less likely in the case of copper. The maximum temperature rise in the copper catalyst probably did not exceed 1°, an amount which was not readily observable with the pyrometric apparatus employed. Just as in the case of nickel, the oxygen inhibited the reduction of the stable oxide formed during the synthesis. The curves show that this oxide like the nickel oxide was rapidly reduced by *pure* hydrogen at the temperature of its formation.

Discussion of Results

The results shown graphically in Figs. 3 and 4 lead to the conclusion that the reactions occurring on nickel and copper are essentially alike. In each case there occurs a sharp rise to a relatively high initial rate of conversion followed by a decrease to a lower steady value. In each case a stable oxide is formed, the reduction of which is inhibited by oxygen. The presence of this stable oxide apparently interferes with some faster reaction. Differences in the actual forms of the curves for these two metals may be explained by differences in the specific activity of the catalysts, their thermal characteristics and the chemical properties of the stable oxides which develop during the synthesis.

These experiments indicate that at least two distinct reactions take place during the catalytic formation of water on nickel and on copper. One of these reactions involves the formation of an oxide (visible in the case of copper) that is not readily reduced by hydrogen if oxygen be present. During the synthesis, therefore, the reduction of this oxide probably contributes little to the total water being formed. The other reaction (or reactions) is most in evidence during the initial period of high activity. It is undoubtedly the faster reaction and as such accounts for the greater part of the water formed, not only initially but also during the period of low activity.

The experimental results so far obtained offer no adequate basis for determining the real mechanism of the (two or more) reactions occurring on copper and on nickel. The reaction involving the stable oxide is no doubt one of alternate oxidation and reduction. However, a much faster reaction is taking place, the nature of which is not so apparent. In this reaction the oxygen may be selectively adsorbed; intermediate oxygen compounds may be formed; or there may be an "incipient oxidation," as suggested for copper by Pease and Taylor.[2] Each of these concepts implies the formation of an "indefinite oxide," a designation which is fully as satisfactory for the needs of this paper. The mechanism of the faster reaction involving this indefinite oxide becomes, then, one of alternate oxidation and reduction, differing essentially from the slower reaction only in the rate with which the alternate oxidation and reduction steps occur.

In discussing the faster reaction which is taking place during the catalytic formation of water, all reference to the action of copper or of nickel on the hydrogen has been avoided purposely. It is, of course, conceivable that some phenomenon such as selective adsorption of both oxygen and hydrogen must occur before combination takes place. And, in the absence of experimental data to the contrary, this possibility ought not to be excluded. Experiments on an evacuated catalyst indicate that activation of the hydrogen is not a prerequisite to this catalysis. It is recognized, however, that these experiments are not conclusive. A further study of the relation of the metal catalyst to the hydrogen is being made in this Laboratory.

The retardation produced by the stable oxide which forms during the water synthesis is very similar to the effect produced by nitrides on iron catalysts during ammonia synthesis (not yet published). The results obtained in the study of these two catalytic reactions suggest that, for a metal catalyst at least, a stable compound (or compounds) may be formed by side reactions and that the presence of this stable compound may effectively decrease the activity of the catalyst. In the case of ammonia catalysts the experiments indicate that the amount or the stability of the nitride accumulation can be decreased by the addition of certain "promoters," the result being a more reactive catalyst. This observation suggested that a proper selection of promoters may decrease the stability of the oxides formed on nickel and on copper. A study of such promoted copper and nickel catalysts is now being made by one of us.

Summary

1. The synthesis of water over reduced nickel and copper catalysts has been studied at temperatures between 34° and 130° and with oxygen concentrations as high as 2%.

2. The nature of the catalytic action has been shown to be essentially the same for both metals. In each case the rate of water formation increased to a maximum and then fell to a steady, lower value. During the period of high activity a stable oxide gradually formed on the catalyst surface which was not readily reduced by hydrogen in the presence of oxygen. In each case this oxide was observed to decrease the catalytic activity of the metal.

3. The experimental results offer no adequate basis for determining the mechanism of the reactions occurring on copper and on nickel. The results suggest that there are at least two distinct reactions taking place, each reaction involving the formation of an oxide and its subsequent reduction by hydrogen. These reactions, therefore, appear to be essentially alike, differing only in the rate with which the alternate oxidation and reduction steps occur.

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