[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

The Nature of the Surface of Catalytic Nickel[1]

BY W. WALKER RUSSELL AND WILLIAM V. LOEBENSTEIN[1a]

Information about the characteristics of a catalyst surface can be obtained by properly devised poisoning experiments. A suitable catalyst poison should make known the possible presence in the catalyst surface of areas or centers possessing different degrees of catalytic activity. This is accomplished if the poison is preferentially adsorbed first upon areas of greatest activity and then upon less and less active areas as poisoning becomes more extensive. Such poisoning is termed selective. Furthermore, the ideal poison should remain intact upon the catalyst surface throughout any reaction velocity measurements, but be capable of complete removal finally for evaluation, and to restore the catalyst surface unchanged for further studies. Russell and Ghering[2] achieved the equivalent of a selective poisoning of copper by first completely poisoning with oxygen, and then selectively removing it by reduction with limited amounts of hydrogen. In the work which follows, nickel catalysts have been subjected to carbon poisoning which may be made selective and capable of disclosing much about the nature of the active surface of the catalysts.

Preliminary Results

A. Preliminary Work on Poisoning by Ethylene Decomposition.—The poisoning of quartz-

supported nickel catalysts by the catalytic decomposition of ethylene at 275° was studied. This temperature is well below 350° where the non-catalytic decomposition of ethylene is still very slow.[3] Increments of ethylene, varying in size but always large enough to produce a residual pressure permanent at room temperature, were admitted to the freshly reduced and evacuated catalyst. The temperature was now slowly raised to 275° and kept there for about seven hours, after which the catalyst was flushed with hydrogen while the temperature was finally raised to 300°, which was 25° below the catalyst reduction temperature. After cooling, the capacity of the poisoned nickel to hydrogenate acetone to isopropyl alcohol at 110° was measured by a flow method. At the end of the measurement the catalyst was thoroughly flushed with hydrogen and finally at 300°, then cooled to 0°, evacuated and oxygen admitted. The amount of poison on the catalyst was considered to be given by the amount of carbon present in the carbon dioxide found when the catalyst was heated to 550° in a stream of oxygen, and the combustion products passed over copper oxide at 800°. This assumes that although the decomposition of ethylene is complex,[4] after a prolonged flushing of the catalyst with hydrogen at 300°, only carbon remains to poison the surface. From a series of measurements, it was found that a selective poisoning was accomplished in that the smallest amounts

(2) Russell and Ghering, THIS JOURNAL, **57**, 2544 (1935).

(3) Storch, *ibid.*, **56**, 374 (1934).

(4) Cantelo. *J. Phys. Chem.*, **31**, 124, 246 (1927).

of carbon produced relatively the largest decreases in catalyst activity. Thus 12 micrograms of carbon reduced the activity of 14.66 g. of quartz carrying 5% nickel by 50%, twice the amount of carbon reduced the activity by 60%, 52 micrograms by 80%, while with 77 micrograms of carbon on the surface the catalyst still possessed 10% of its initial activity. Since, during the ethylene decomposition and subsequent treatment with hydrogen at 300° all portions of the catalyst surface had equal opportunity to be poisoned, the non-linear relation found above indicates that the nickel surface was not uniform in catalytic activity. Certain parts of the nickel preferentially decomposed ethylene, and these included portions of the catalyst which were more active than others in the hydrogenation of acetone.

B. Preliminary Work on Poisoning by Methane Decomposition.

Active nickel both decomposes methane[5] and smoothly catalyzes methane formation from carbon dioxide and excess hydrogen at temperatures between 300 and 400°. Thus, it appeared possible to poison a nickel catalyst at high temperatures by the selective deposition of carbon from methane produced *in situ*, and then to measure the catalyst activity by its capacity to hydrogenate carbon dioxide at a lower temperature. Such a dual use of the hydrogen–carbon dioxide reaction was found possible by decomposing the methane formed at 500° and evaluating the hydrogenating capacity of the catalyst at 315°. Repeated methane decompositions in a static system progressively poisoned the catalyst until it possessed about 60% of its initial activity. Much more complete poisoning, however, could be produced by slowly passing the theoretical 1 to 4 carbon dioxide, hydrogen mixture over the catalyst at 500°. Such poisoning was slowly removed in a stream of pure hydrogen at 500°, or more rapidly by oxidation.

Apparatus and Experimental Method

Apparatus.—The apparatus which was used in the main body of the work was all Pyrex glass with the exception of the catalyst tube, which was of transparent quartz. This tube, which was 20 cm. long and 25 mm. wide, occupied the midportion of a horizontal, insulated and electrically heated tube space some 46 cm. long, which was wound in three sections in order to offset temperature gradients in the catalyst. In the catalyst tube 88.2 g. of quartz-

(5) Morikawa, Trenner and Taylor, THIS JOURNAL, **59**, 1103 (1937).

supported nickel was held between wads of silica cotton. The temperature of the catalyst was measured by an external thermometer or thermocouple about the center of the catalyst mass. By means of graded seals, one end of the catalyst tube led to the analysis system, the other to the gas purification system, flowmeters, mercury diffusion pump (protected by a liquid-air trap) and McLeod gage. Purified mineral oil was used in the calibrated flowmeters.

Purification of Gases.—Compressed, electrolytic hydrogen was purified by passage over platinized asbestos at 350°, thoria-promoted nickel at 290°, ascarite, calcium chloride and phosphorus pentoxide. High grade compressed carbon dioxide, and nitrous oxide were given a preliminary purification which comprised passage through a trap cooled by dry-ice and alcohol, then over calcium chloride. In the reaction velocity measurements the hydrogen–carbon dioxide mixture was further purified by passage at room temperature over a pumice-supported, thoria-promoted nickel catalyst sintered enough not to catalyze any interaction between the gases which then passed over phosphorus pentoxide and to the main catalyst. The nitrous oxide–hydrogen mixture for the reaction velocity measurements was further purified only by passage over phosphorus pentoxide.

Preparation of Catalyst.—The catalyst consisted of 5% nickel supported on granulated quartz. Large quartz crystals were crushed, and the 20 to 40 mesh portion purified by repeated extractions with hot concentrated nitric acid. After washing, the granules were dried at 110°, ignited at 800° in an electric muffle, and cooled in a desiccator. To 122 g. of the purified quartz granules in a porcelain casserole, there was added 30.26 g. of pure nickelous nitrate crystals dissolved in enough water to moisten the quartz thoroughly. By gentle heating and stirring, the mass was caused to dry uniformly. Increased heating now caused the evolution of oxides of nitrogen. During the final heating with a Meker burner, the mass was stirred as little as possible in order to avoid dislodgment of the nickel oxide coating. Of this catalyst mass, 88.2 g. was introduced into the quartz reaction tube. The activity of the catalyst was stabilized by a series of fourteen alternate oxidations with oxygen at 1020° and reductions with hydrogen first at 275° and then at 550°, carried out in the latter part of the preliminary work.

Procedure for Reaction Velocity Measurements.—The reaction velocity runs were made by first adjusting the hydrogen flow through the catalyst to the rate required in the run. Within an hour, the catalyst temperature was regulated and the carbon dioxide or nitrous oxide metered into the hydrogen stream at the rate of 6.74 cc. per minute. The hydrogenation of carbon dioxide was carried out at 315°, unless otherwise specified, using a 6 to 1 mixture of the former to the latter gas, and thus a 50% excess of hydrogen. The hydrogenation of nitrous oxide was carried out at 73.5° using a 4 to 1 mixture, and, therefore, a 100% excess of hydrogen, inasmuch as the reaction products were solely nitrogen and water. It was found that no ammonia appeared in the reaction products below 170°. After the reaction mixture had passed through the catalyst for an hour, the water produced in the reaction products in successive fifteen-minute intervals was collected in a

phosphorus pentoxide tube and weighed. For this time interval with complete hydrogenation the nitrous oxide furnished 81.6 mg. of water, while the carbon dioxide furnished 160.7 mg. When it was desired to obtain information as early as possible during a run, and this was the case for the runs shown in Fig. 2, the catalyst, while still sealed off in hydrogen, was brought to the reaction temperature. Meanwhile, by bypassing, the desired gas composition and rate of flow could be established in the system right up to the catalyst tube entrance. In this manner, water absorptions could be started almost as soon as the reaction mixture passed through the catalyst. The time of a water absorption was taken as the middle of the time interval during which water was collected. Measurements were continued for an hour or more until the activity of the catalyst surface had been established. At the end of a run, the catalyst surface was flushed with hydrogen for an hour before the catalyst temperature was allowed to change.

Poisoning Procedures.—The catalyst was deliberately poisoned by either of two procedures. The smaller degrees of poisoning could be produced by a static method in which the catalyst was isolated and heated at 500–510° with a limited amount of a 1 to 4, or 1 to 6 carbon dioxide–hydrogen reaction mixture for one or more hours. Larger amounts of poisoning could be produced by causing either of the above reaction gas mixtures to flow at 30 to 40 cc. per minute while the catalyst temperature was slowly raised to 500–510°, held there from one to seven hours, then dropped in the course of an hour or so to 350–320° with no interruption of gas flow. Then the carbon dioxide was cut off and hydrogen alone allowed to flush the catalyst surface for an hour before cooling further. The flow method of poisoning was used exclusively in the main body of the work.

Activation Procedures.—After poisoning, the catalyst was activated by either of two procedures. In the so-called "hydrogen" activation, after the catalyst had been flushed with hydrogen for an hour at the temperature of the previous run, it was heated to 500° in the course of an hour. Here it was maintained for definite periods of time up to fifteen hours in a hydrogen flow of 27 cc. per minute.

It was accidentally found that poisoned catalysts could also be activated by raising the catalyst temperature slowly to 500°, while the carbon dioxide–hydrogen reaction mixture was passed, as in the flow method of poisoning above described, provided that the catalyst was then completely cooled in the static reaction mixture. Thus, after two hours at 500°, the catalyst was isolated quickly from the rest of the system and caused to cool (by opening the furnace) to room temperature in the static gas mixture. The catalyst was flushed with hydrogen, first cold, and then as the temperature was raised to that of the reaction velocity run. This so-called "methane mixture" activation was very effective and much more rapid than the "hydrogen" activation.

Experimental Results

A. Deliberate Poisoning and Activation.—The activity of the nickel catalyst, when poisoned to various different extents, was measured by its capacity to hydrogenate separately both carbon dioxide and nitrous oxide. In Fig. 1 there are shown graphically 38 successive reaction velocity runs. In general, the plan here was to evaluate a catalyst surface by two carbon dioxide hydrogenations at 315° with an intervening nitrous oxide hydrogenation carried out at 73.5°. The catalyst surface was then poisoned by the decomposition of methane produced *in situ* at 500° or was deliberately activated, and its hydrogenating capacity again measured. In Fig. 1, mg. of water per fifteen-minute interval, yielded by either hydrogenation, is plotted vertically against a horizontal chronological sequence of reaction velocity runs. In this figure, the positions of the letters on the graphs indicate between which runs the deliberate poisonings, P, and activations, A, were made. The letter A signifies a "hydrogen" activation, A' a "methane mixture" activation. The solid lines trace the changes in the catalyst's capacity to hydrogenate carbon dioxide, while the dotted lines give similar information with respect to the hydrogenation of nitrous oxide. It is immediately clear that large changes in the capacity of the nickel catalyst to hydrogenate carbon dioxide were accompanied by smaller changes, even of opposite sign, in the catalyst's capacity to hydrogenate nitrous oxide. However, the catalyst surface, when the fourth nitrous oxide hydrogenation was made, appears to have been temporarily additionally poisoned in some unknown manner so that this point is undoubtedly somewhat too low.
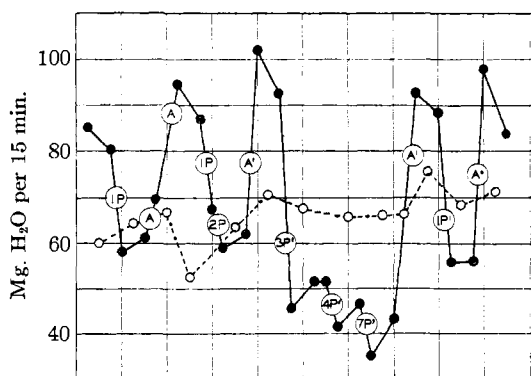
Chronological order of successive runs.

Fig. 1.—Poisonings and activations produced in thirty-eight successive hydrogenations of carbon dioxide (solid circles) and of nitrous oxide (open circles), respectively. Curve letters: A, "hydrogen" activation; A', "methane mixture" activation; nP, *n* hours of poisoning by methane decomposition.

Since the carbon dioxide hydrogenations shown in Fig. 1 proceeded smoothly without self-

poisoning, it was possible to obtain temperature coefficient data from reaction velocity measurements at 300° and 315°. Such data were obtained for the catalyst poisoned to different extents. The following temperature coefficients (per 15° temperature interval), each followed by the activity of the surface to hydrogenate carbon dioxide at 315° as mg. of water per fifteen-minute interval, in brackets, were found: 1.62 (88.3 mg.); 1.63 (83.8 mg.); 1.65 (79.0 mg.); 1.67 (46.1 mg.); 1.66 (41.3 mg.). Although the differences between the temperature coefficients are small and of the order of the experimental error, the largest values of the coefficient occur on the most poisoned surfaces, as would be expected. However, the complexity of the temperature coefficient of heterogeneous catalytic reactions is such that the very small observed change in this coefficient, as poisoning increased, can hardly be interpreted as evidence for the uniformity of the catalytic surface of the nickel. Although, in the nitrous oxide hydrogenations shown in Fig. 1, self-poisoning was slight and easily allowed for, no temperature coefficient data were obtained for this reaction.
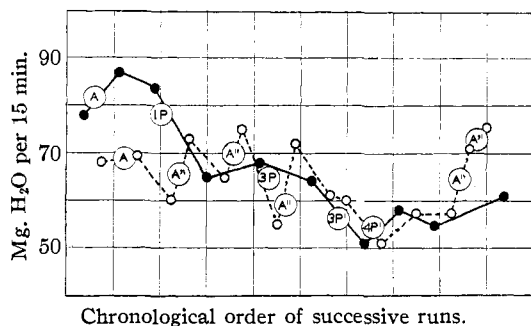

Chronological order of successive runs.

Fig. 2.—Poisonings and activations produced in twenty-five successive hydrogenations of carbon dioxide (solid circles) and of nitrous oxide (open circles), respectively. Curve letters: A, "hydrogen" activation; A″, nitrous oxide–hydrogen activation; nP, n hours poisoning by methane decomposition.

In Fig. 2, the experimental results are portrayed in a manner similar to Fig. 1. However, after a deliberate poisoning or activation, the capacity of the catalyst to hydrogenate nitrous oxide was always measured first. In the twenty-five successive reaction velocity measurements shown in this figure, nitrous oxide hydrogenations predominate. Also, the run sequences are such that the catalyst's capacity to hydrogenate nitrous oxide is varied more frequent'y and its capacity to hydrogenate carbon dioxide less widely

than in Fig. 1. In both of these figures, the numbers preceding the letter P indicate the duration of the poisoning treatment in hours at 500°. The letter P′ indicates that after the poisoning the catalyst was flushed with hydrogen at about 320° instead of 350°. It is at once apparent that catalyst surfaces most active in hydrogenating carbon dioxide were most easily poisoned, while surfaces already considerably poisoned were further poisoned only by long exposure to poisoning conditions.

B. Non-deliberate Poisoning and Activation.—Other no less definite and no less reproducible catalyst changes took place as a result of the occurrence on the catalyst surface of the hydrogenations studied, and of the definite sequences of experimental manipulations employed. Such non-deliberate changes in catalyst activity are clearly evident in both Figs. 1 and 2. In Fig. 1 it is seen that the occurrence of the hydrogenation of nitrous oxide upon the catalyst surface changed the capacity of the surface for hydrogenating carbon dioxide. Thus, an intervening nitrous oxide hydrogenation either caused further poisoning, or an activation of the catalyst for the hydrogenation of carbon dioxide, depending upon whether the catalyst was initially relatively little, or rather considerably, poisoned for this hydrogenation. The effects are shown graphically in Fig. 1 by the fact that the peak tips slope down to the right (poisoning), while the valley bottoms slope upward toward the right (activation). Furthermore, if the capacities of the catalyst surfaces to hydrogenate carbon dioxide are plotted against the changes, e. g., poisoning considered negative and activation positive, in catalyst capacity caused by an interposed nitrous oxide hydrogenation, the data from Fig. 1 produce an approximately linear relation. This could hardly occur except the quality of the surface of the nickel varied from place to place in a regular manner.

The catalyst surfaces under study in Fig. 2 proved to be quite susceptible to self-poisoning during a hydrogenation run, particularly in the case of nitrous oxide. Therefore, in all the reaction velocity runs shown in Fig. 2, the measurements were started five minutes after the desired reaction gas mixture had entered the temperature-regulated catalyst chamber. All measurements in this figure are extrapolated back to zero time on the basis of 4 or 5 observed values. The letters P and

A on the curves in Fig. 2 have their same significances, but A″ designates another type of activation, observed when, after completing a nitrous oxide hydrogenation, the catalyst was flushed with hydrogen, then heated at 315° in a hydrogen stream for an hour, and the nitrous oxide hydrogenation repeated at 73.5°. Five instances of such catalyst activation for nitrous oxide hydrogenation which could be produced at will are seen in Fig. 2. It is clear that not only was any self-poisoning that took place during a nitrous oxide hydrogenation removed, but, in addition, activation occurred, which was the greater the less the initial capacity of a surface to hydrogenate nitrous oxide. Thus, if the zero time capacity of a surface to hydrogenate nitrous oxide is plotted against this capacity after the hydrogen treatment, a smooth curve results. Such a curve is useful in predicting the capacity of a surface to hydrogenate nitrous oxide at the time when its capacity to hydrogenate carbon dioxide is being actually measured. This was the case whenever in the work the hydrogenation of carbon dioxide at 315° followed directly that of nitrous oxide at 73.5°, since then such an activation of the catalyst surface for the latter reaction was involved. When a carbon dioxide hydrogenation was interposed between two nitrous oxide hydrogenations, although the activation must have occurred, it is in all cases but one in Fig. 2 masked by some poisoning of the activated surface by the occurrence of the carbon dioxide hydrogenation. However, if the change in catalyst capacity to hydrogenate nitrous oxide, caused by an intervening carbon dioxide hydrogenation, is referred to the *first* nitrous oxide hydrogenation on a surface, an increase in activity toward the latter hydrogenation is found in three cases with no change in two cases in Figs. 1 and 2.

C. **Selectivity of Poisoning and Activation.—** It may be inquired how the ratio of the capacity of the catalyst to hydrogenate carbon dioxide to its capacity to hydrogenate nitrous oxide changed during the large number of poisonings and activations, both deliberate and non-deliberate, produced upon the catalyst. Wherever in the work a carbon dioxide hydrogenation is followed directly by the hydrogenation of nitrous oxide, a quality ratio can be computed. The ratio of the capacity of the catalyst to catalyze the hydrogenation of carbon dioxide at the end of the run to the zero time capacity of the surface to catalyze the hydro-

genation of nitrous oxide defines the surface produced by the deliberate treatment preceding the carbon dioxide hydrogenation plus any changes in catalyst surface caused by the occurrence of the latter reaction and not removed by flushing with hydrogen at 315°. No change in catalyst activity is to be anticipated upon cooling from 315 to 73.5°, the temperature of nitrous oxide hydrogenation. The quality ratio directly computed from the capacity of the catalyst to hydrogenate nitrous oxide at the end of a run and the zero time value of a directly following carbon dioxide hydrogenation, however, will be in error due to the activation of the catalyst for the former reaction which occurred after this reaction was completed and while the catalyst was being heated in hydrogen to 315° prior to the carbon dioxide hydrogenation. From the curve mentioned in preceding Section B, however, it is possible to predict the capacity of a surface to hydrogenate nitrous oxide at the time its carbon dioxide hydrogenating capacity is measured by knowing the catalyst's zero time capacity to hydrogenate nitrous oxide in the directly preceding run. Such corrected quality ratios define a surface produced by the deliberate treatment preceding the nitrous oxide hydrogenation plus any changes in catalyst surface occurring during the run and the subsequent activation preceding the carbon dioxide hydrogenation. In Fig. 3, quality ratios, *i. e.*, hydrogenating capacity for carbon dioxide to that for nitrous oxide, are plotted vertically while the capacity of the surface to hydrogenate carbon dioxide, expressed as mg. of water per fifteen-minute interval, is plotted horizontally. The open circles designate quality ratios, in which the nitrous oxide hydrogenation occurred first upon a surface and which, therefore, have been corrected as above mentioned. The solid circles indicate quality ratios requiring no correction. In Fig. 3, the quality ratios taken from all parts of the work and, therefore, representing the catalyst in many states of activity, are assembled. The heavy Curve 1 is the best straight line (method of least square errors) possible through the experimental points.

The manner of presenting data used in Fig. 3 leads to the consideration of three limiting cases. If the catalyst surface were uniform in that all parts were equally effective in catalyzing both of the hydrogenations studied, or if the catalyst surface were not uniform yet the poisoning were
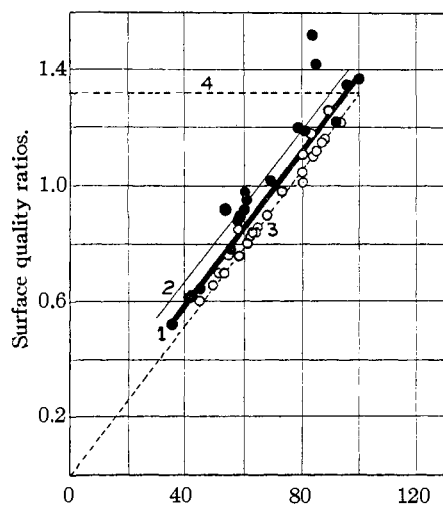
Fig. 3.—Selectivity of poisonings and activations. Curve 1, corrected experimental points; Curve 2, uncorrected experimental points; Curve 3, theoretical curve for selective poisoning only of surface catalyzing carbon dioxide hydrogenation; Curve 4, theoretical curve for non-selective poisoning or uniform catalyst surface.

non-selective in that it poisoned equally types of surface which catalyzed the two hydrogenations with quite different efficiencies, a horizontal line (Curve 4) passing through the quality ratio of the least poisoned surface should be the locus of the experimental points. Second, if the portions of the surface which catalyzed the hydrogenation of carbon dioxide escaped poisoning entirely, while those surface types active in nitrous oxide hydrogenation were exclusively poisoned, the experimental ratios should fall on a straight line passing vertically upward through the quality ratio of the least poisoned surface. Third, if those portions of the surface which catalyzed the hydrogenation of nitrous oxide were not poisoned while those surface types catalyzing the carbon dioxide hydrogenation were exclusively poisoned, the locus of the experimental points should be a straight line (Curve 3 in Fig. 3) passing through the origin of coördinates and the quality ratio point of the least poisoned surface, and in the present case have a slope of 0.0132. Curve 1, the best straight line through the experimental data, has a slope of 0.0131 and, therefore, lies parallel to Curve 3. Its extrapolated intercept on the quality ratio axis is 0.076 so that it passes close to the point representing the least poisoned surface, i. e., the intersection of Curves 3 and 4. Furthermore, the order in which the experimental points appear on Curve 1 is very far from that in which they

were obtained so that no permanent selective poisoning of the catalyst occurred. Although the necessity of correcting those quality ratios computed from consecutive runs in which nitrous oxide was hydrogenated first has been pointed out, it is of interest to consider the consequences of omitting this correction. The thin Curve 2 is the locus of all experimental points, with no correction made to any quality ratios, and is seen to lie close to Curve 1. Therefore, whether the correction is applied or not, there is no doubt that the experimental data fall predominantly in the third class considered. The fact that, although Curves 1 and 2 lie close to Curve 3, they are always above it, may be due to determinate experimental error, to lack of complete specificity in the poisonings and/or activations, and/or the existence of some catalyst surface capable of catalyzing both the hydrogenation of carbon dioxide and of nitrous oxide. Simple direct poisoning by methane decomposition is surely not completely selective.

General Discussion

In a study of the type here undertaken, it is of the first importance that all treatments which can alter the activity of the catalyst be of such a nature that all parts of the catalyst mass and surface have equal opportunity to react at the same time. In a static system, an excess of reagent may be admitted below reaction temperature, after which heat is applied. Where a flow method of treatment is adopted, e. g., to secure greater poisoning, it is essential that reaction occur slowly with respect to the rate of flow so that all portions of the catalyst are at all times in contact with reactants of essentially the same composition. It is believed that these conditions were met during the present work.

It may be assumed that the poisoning caused by methane decomposition was due to the deposition of carbon upon the catalyst surface, since nickel carbide is reported to be unstable[6] above 420°. "Hydrogen" activation can then be considered a simple reversal of the poisoning reaction. The more rapid and efficient "methane mixture" activation differed from the procedure of poisoning the catalyst by methane decomposition only in that the catalyst was finally cooled from 500° in a static instead of a flowing reaction mixture. When the reaction mixture was

(6) Scheffer, Dokkum and Al, Rec. trav. chim., 45, 803 (1926).

evacuated from the catalyst chamber at 500° before cooling, poisoning and not activation resulted. Since the most poisoned catalyst still possessed about a third of its initial capacity to hydrogenate carbon dioxide at 315°, it must be assumed that at 500° methanation was always essentially complete. It seems necessary to attribute the activation which occurred in the static cooling of the catalyst to the water vapor present and to the long times of contact available. Although the reaction of steam and carbon is ordinarily slow below 600°, in the presence of catalytic nickel in which the deposited carbon may be rather reactive, and with the products carbon monoxide and hydrogen disappearing via the water gas or methanation reactions which proceed rapidly down to 300° and lower, the primary reaction may well be considerably accelerated.[7]

The occurrence of nitrous oxide hydrogenation upon a nickel surface at 73.5°, which was then heated to 315° in a stream of hydrogen, has been shown capable of altering the catalytic activity of the nickel both for the hydrogenation of carbon dioxide and of nitrous oxide. Such changes appear consistent with the concepts which follow. When nitrous oxide alone is brought into contact with catalytically active metals, such as nickel, it is easily decomposed to form adsorbed oxygen which may include some surface oxide. In the presence of hydrogen, nitrous oxide hydrogenation will then occur on those portions of the surface which carry adsorbed oxygen reducible under the experimental conditions, and these surface portions should be the more extensive the higher the temperature. The further poisoning of nickel for carbon dioxide hydrogenation, by hydrogenating nitrous oxide on the nickel surface, may then be attributed to the formation of some adsorbed oxygen (oxide) at 73.5° which proved irreducible at 315°. The activation of nickel, which was considerably poisoned deliberately, for the hydrogenation of carbon dioxide by an intervening nitrous oxide hydrogenation, would be explained by the removal of less strongly adsorbed carbon poisoning by interaction with adsorbed oxygen in the presence of hydrogen at 315°. Only nickel poisoned to give less than about 70 mg. of water from carbon dioxide hydrogenation appeared capable of undergoing activation during a single nitrous oxide hydrogenation. Similarly, the activation of nickel for the hydro-

(7) Taylor and Neville, THIS JOURNAL, **43**, 2055 (1921).

genation of nitrous oxide caused by heating the surface to 315° in hydrogen after a preceding like run may be attributed to the removal of carbon poisoning by interaction with adsorbed oxygen.

The preliminary work with ethylene poisoning, and the work just discussed, clearly require the catalytic surface of nickel to be of non-uniform activity. Nickel which no longer decomposed ethylene to carbon under the experimental conditions was still active at a lower temperature in hydrogenating acetone. Similarly, after methane decomposition became negligibly slow at 500° (lowest point in Fig. 1), the nickel had lost only about 9% of its activity for the hydrogenation of nitrous oxide at 73.5° and about 65% of its capacity to hydrogenate carbon dioxide at 315°. The hydrogenations, therefore, proceed in part upon different and presumably less active surface than the decomposition reactions. The hydrogenation of nitrous oxide occurs upon surface which is different from, and presumably less active than, surface catalyzing the decomposition of methane and carbon dioxide hydrogenation. The preferential removal of carbon from surface catalyzing the hydrogenation of nitrous oxide by heating with oxygen adsorbed during a previous like run indicates that the nickel surface was not uniform in its tenacity in holding adsorbed carbon. Poisoning by methane decomposition followed by such a preferential removal of carbon constituted the most selective method of poisoning the carbon dioxide hydrogenating surface. This is shown graphically by the better agreement of the open circles with Curve 3 of Fig. 3. As was shown in Fig. 3, the behavior of the quality ratios is clearly consistent with the concept that the nickel surface capable of being selectively poisoned for the hydrogenation of carbon dioxide was not the surface which catalyzed the hydrogenation of nitrous oxide. It is concluded that, under the conditions of study, the nickel surface responsible for catalyzing about two-thirds of the carbon dioxide hydrogenated was exclusive of nickel surface catalyzing the hydrogenation of nitrous oxide, and that there is nothing in the present investigation to preclude the possibility that these two hydrogenations proceed entirely upon mutually exclusive types of nickel surface.

Summary

1. Quartz supported nickel catalysts have been progressively and selectively poisoned by the

catalytic thermal decomposition of (a) ethylene for the hydrogenation of acetone at 110°, (b) methane for the hydrogenation of carbon dioxide at 315°, and of nitrous oxide at 73.5°

2. The experimental evidence indicates that the surface of the nickel catalysts studied was non-uniform because (a) catalysts which no longer catalyzed the decomposition reactions were still active at lower temperatures in the hydrogenation reactions, (b) certain parts of the

surface were more active than others in the hydrogenation of acetone, (c) heating in hydrogen a surface upon which the hydrogenation of nitrous oxide had occurred caused selective activation or poisoning according to conditions, (d) the nickel surface responsible for about two-thirds of the hydrogenation of carbon dioxide could be poisoned without affecting the nickel surface which catalyzed the hydrogenation of nitrous oxide.

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An Electrophoretic Study of the Proteins of Egg White

By Lewis G. Longsworth, R. Keith Cannan and D. A. MacInnes

Due to its availability, its importance in nutrition, and as a source of proteins for biological investigations, egg white has been the subject of many researches.[1] As the result of much painstaking work, the number and relative amounts of the major components of that material have been ascertained. With the advent of the electrophoretic method, as improved by Tiselius,[2] it has, however, been possible to obtain much additional quantitative information regarding this very complex protein system. Up to the present time the only electrophoretic study of egg white that has been published is that of Young,[3] who used the original Tiselius apparatus which yielded simple schlieren bands. He reported "five or six separate migrating boundaries" at pH 7.2. With the addition of the scale method of Lamm,[4] the diagonal schlieren method of Philpot,[5] and Svensson,[6] or the schlieren scanning method developed in this Laboratory,[7] and described in detail in a recent article,[8] it is possible to obtain, in addition to the number and mobilities, data concerning the concentrations of the constituents present. In the research to be described below the schlieren scanning method was used. In all, 134 separate electrophoretic experiments were made on egg white and its

constituents and considerably more than that number of electrophoretic patterns were obtained. In the following only representative or typical patterns can be shown, but all of the results are consistent with the interpretation we have given.

With the exception of two modifications: i. e., a double length section of the electrophoresis cell, and a cell support, to be described below, the electrophoresis apparatus used has remained as outlined in recent articles from this Laboratory.[8,9,10] The double length section, II, is shown in position in the support in Figs. 1-a and 1-b. This section fills most of the field of the schlieren lens, without the disturbing horizontal glass plates obscuring the middle of the field, as in the more usual four section apparatus. With this arrangement it is possible to spread the boundaries over more than twice the distance, with the possibility of finding more detail in the electrophoretic patterns.[11] The filling of the apparatus, however, involves a somewhat different procedure than with the older type of cell and is as follows. As before, boundaries are initially formed between a buffer solution in which a protein is dissolved, and the buffer itself. The protein bearing solution is placed in the bottom section, III, the filling extending somewhat into section II. The bottom section is isolated by pushing it to the left. The

(1) The early researches on egg white have been excellently summarized by Hektoen and Cole, *J. Infectious Diseases*, **42**, 1 (1928).

(2) Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

(3) Young, *J. Biol. Chem.*, **128**, cxiv (1939).

(4) Lamm, *Nova Acta Regiae Soc. Sci. Upsaliensis*, Ser. IV, **10**, No. 6 (1937).

(5) Philpot, *Nature*, **141**, 283 (1938).

(6) Svensson, *Kolloid-Z.*, **87**, 181 (1939).

(7) Longsworth, This Journal, **61**, 529 (1939).

(8) Longsworth and MacInnes, *ibid.*, **62**, 705 (1940).

(9) Longsworth, *Ann. N. Y. Acad. Sci.*, **39**, 187 (1939).

(10) Longsworth and MacInnes, *Chem. Rev.*, **24**, 271 (1939).

(11) The double length section was suggested to us by Prof. Arne Tiselius before his return to Sweden. Although most of the results to be outlined in this paper were obtained before the new sections were available they have been used in all our recent work, and we regard them as a distinct contribution to the electrophoretic technique.