of E_0 in this case. If it is assumed that the Debye–Hückel equation[4]

$$-\log \gamma = \frac{2.96\ Z_1Z_2\ \sqrt{\mu}}{1 + .592 \times 10^8\ a\ \sqrt{\mu}}$$

with a reasonable value of the ion diameter is applicable to these solutions a value of E_0 may be calculated from each experimental measurement. The constancy of these values indicates the validity of the assumptions made. In columns five and six of Table I values of $-\log \gamma$ and of the corresponding E_0 are listed. These calculations were made with a value of 2.5×10^{-8} cm. for the ion diameter. In the figure the solid curve represents a plot of E_0' calculated from the values of $-\log \gamma$ and the value of 0.420 for E_0. The slope of the limiting law is also indicated on the figure. As may be seen from the figure and also from Table I the calculated and experimental values are in reasonably good agreement in the dilute solutions except for the first point.

Since the dissociation of the second hydrogen ion from sulfuric acid is not complete even in water solutions it might reasonably be assumed to be even less so in the solutions of alcohol. The limiting case would of course be one in which only the primary dissociation would be considered. The equation for the electromotive force, from this point of view, becomes $E = E_0 - (2RT/2F) \ln \gamma M$ and the ionic strength is equal to the concentration. Calculations from this point of view were made using the extended equation of Gronwall, La Mer and Sandved,[5] and an assumed ion diameter of 1.7×10^{-8} cm. The shaded circles of the figure represent the experimental points, the full curve the calculated values and the straight line the limiting law on this basis. Results of these calculations showed that the equation is not convergent for this small ion diameter in alcohol. However, a larger value for the ion diameter would not be in agreement with the experimental values.

Since the experimental curve lies above the limiting law in dilute solutions it is obvious that the application of the first approximation of Debye and Hückel will not account for the experimental curve. Although the extended equation does give constant values for E_0 on this basis the significance of this is perhaps questionable in view of the non-convergence of the series.

Summary

Activity coefficients of sulfuric acid solutions in ethyl alcohol have been determined by measurement of the cell H_2, H_2SO_4, $Hg_2SO_4(s)$, Hg. The data have been treated by the Debye–Hückel equation and by the extended equation of Gronwall, La Mer and Sandved.

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[4] The constants in this equation were evaluated using for the dielectric constant of ethyl alcohol the value of 24.20 as given by Åkerlöf [THIS JOURNAL, **54**, 4126 (1932)].

[5] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928). For alcohol solutions at 25° the constants become, +5.00, −5.30 and −28.11.

STATE COLLEGE, PENNSYLVANIA RECEIVED AUGUST 5, 1935

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

The Nature of the Surface of Copper Catalysts

BY W. WALKER RUSSELL AND LEONARD G. GHERING[1]

Experimental evidence concerning the nature of catalytic surfaces is conflicting. Kinetic measurements are in general consistent with the concept of a uniformly active catalytic surface, while adsorption phenomena for the most part require a surface of non-uniform nature. This apparent conflict would largely disappear were it found that the reaction catalyzed proceeded predominantly on a relatively few surface types out of many existing on a surface. It is well recognized that a knowledge of the different qualities of catalytic surface present and their distribution is vital to any theory of the catalytic surface or mechanism of catalysis.

By studying the changes in catalytic activity produced by controlled, selective poisoning, much can be learned about the nature of a catalyst surface. Studies have been made of synthetic ammonia catalysts[2] using oxygen and water as poisons; of thoria as a catalyst using water and acetaldehyde to poison the decomposition of

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[1] Metcalf Fellow in Chemistry at Brown University.

[2] J. A. Almquist and C. A. Black, THIS JOURNAL, **48**, 2814 (1926); J. A. Almquist, *ibid.*, **48**, 2820 (1926); P. H. Emmett and S. Brunauer, *ibid.*, **52**, 2682 (1930).

ethyl alcohol;[3] and of platinum[4] employing mercury ions as poison for hydrogen peroxide decomposition and for hydrogenation of several unsaturated organic compounds in the liquid phase. In this last work the activity of the catalyst was found to decrease in a linear manner as the extent of poisoning increased, and this has been interpreted to mean that the catalytic surface of platinum is predominantly uniform in character.

Previous work[5] had shown oxygen to be strongly sorbed by active copper catalysts, and since the heats of sorption decreased with increasing sorption, at least some selectivity in the sorption process was to be anticipated. Furthermore, sorbed oxygen was known[5] to be capable of completely suppressing the hydrogenating activity of copper at 0° and yet to be easily removed by subsequent reduction at higher temperatures. Because of these facts, it was decided to use oxygen as a poison in the study of the nature of the catalyst surface which the well-known ethylene–hydrogen reaction finds active at 0°. Although ease of manipulation has caused this reaction to be employed frequently in a static system, a flow method has been used throughout the present work in order that the results should be free from errors due to adsorption, induction periods,[6] transitory fluctuations in catalytic activity,[7,8] and the like. The principal significance of the work which follows lies in its elucidation of the nature of the surface of catalytically active copper in the light of three different methods of oxygen poisoning as well as measurements of heats of oxygen sorption.

Apparatus and Experimental Method

Apparatus.—The apparatus used in the controlled poisoning of the catalysts was similar to that used earlier[9] except that provision was now made for admitting gases to either one or both ends of the catalyst bulb. The reaction velocity measurements necessitated ethylene and hydrogen flow-meters which were cut in ahead of the catalyst bulb and trap. These flow-meters were filled with dibutyl phthalate. To the exit tube of the catalyst bulb there was attached a constant-head gas collecting buret[10] so designed that measured volumes of the exit gases could be collected without producing any disturbance of gas flow in the system.

The Bunsen ice calorimeter used for the thermal measurements was essentially of the type already used by others[11] except that the capillary was permanently sealed in place and the stopcock and mercury reservoir for adjusting the position of the mercury thread were omitted. Also, because the calorimeter construction prevented direct observation of the ice mantle, an indicator manometer was temporarily attached to the outer end of the capillary during the formation of the mantle. After a quick movement of the manometer mercury signaled the formation of a mass of ice crystals, heat was introduced until the original manometer reading was nearly reached thus leaving but a few ice nuclei. Upon cooling a second time the mantle formed slowly and the amount of mercury in the calorimeter was such that a suitable mantle thickness was obtained when the mercury thread was well out on the scale. Otherwise the method of using and calibrating the calorimeter was the same as before.[5]

Preparation and Purification of Gases.—The treatment of the helium, hydrogen and oxygen was the same as already described[9] except that in the reaction velocity measurements the hydrogen was further purified by passage over a thoria promoted nickel scrubbing catalyst heated to 250°. Cylinder ethylene was passed at room temperature over a similar scrubbing catalyst after first going through activated charcoal at about 25°. After metering, both gases were further dried and mixed in a tube containing anhydrone and then passed through a trap cooled with solid ammonia before admission to the catalyst. Cylinder nitrous oxide was purified by passing through caustic potash solution, calcium chloride, phosphorus pentoxide and then into a liquid air trap from which only the middle raction was used.

Preparation of Catalysts.—Granular copper catalysts were prepared by sifting Kahlbaum granular cupric oxide "for analysis" so as to retain only particles of about 2–4 mm. diameter, and then reducing slowly with hydrogen at 250°. Cu XXI weighed 36.28 g. Cu XXII was produced by again reducing Cu XXI after accidental admission of air to the latter at 180°. Cu XXII proved more active yet sorbed somewhat less oxygen than Cu XXI. Cu XXIII and Cu XXV were approximately half portions of Cu XXII and weighed 19.83 g. and 16.45 g., respectively. Cu XXIV was produced from Cu XXIII by sintering the latter at 400°.

Procedure for Reaction Velocity Runs.—The reaction velocity runs were made, on either poisoned or unpoisoned surfaces, by admitting hydrogen to the evacuated catalyst at 0° and immediately displacing it with the metered, one-to-one ethylene–hydrogen reaction mixture at a constant rate of flow, *e. g.*, 10 to 20 cc. per minute. Zero time was taken as the instant of admitting the reaction mixture, and after five minutes the conversion was computed from the flow meter readings and the time required to collect 10 or 20 cc. of exit gases. Similar data were taken at ten-minute intervals for from one and one-half to two hours, the period of the run. At the end of the run the catalyst was flushed with hydrogen at 0° for half an hour, and then

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[3] E. K. Rideal and G. I. Hoover, THIS JOURNAL, **49**, 104 (1927).

[4] E. B. Maxted and G. J. Lewis, *J. Chem. Soc.*, 502 (1933); E. B. Maxted and V. Stone, *ibid.*, 672 (1934).

[5] W. W. Russell and O. C. Bacon, THIS JOURNAL, **54**, 54 (1932).

[6] E. K. Rideal, *J. Chem. Soc.*, **121**, 309 (1922).

[7] G. Harker, *J. Soc. Chem. Ind.*, **51**, 323T (1932).

[8] E. G. Insley, *J. Phys. Chem.*, **39**, 623 (1935).

[9] W. W. Russell and L. G. Ghering, THIS JOURNAL, **55**, 4468 (1933).

[10] L. G. Ghering, Thesis, Brown University, 1935.

[11] M. J. Marshall and H. E. Bramston-Cook, THIS JOURNAL, **51**, 2019 (1929).

heated slowly to the temperature of reduction at which the hydrogen flow was continued for the necessary time. The catalyst was then evacuated.

Direct Oxygen Poisoning.—In order to obtain reliable and reproducible catalyst activities with this and the other methods of poisoning, it was necessary to employ a strictly standardized method of procedure. The well-evacuated catalyst was cooled to 0°, a small amount of helium added, and then an accurately measured amount of oxygen was admitted slowly in small increments to both ends of the catalyst bulb. As previously found[5] the oxygen was instantaneously, completely and irreversibly sorbed until saturation of the surface was closely approached. Then sorption became less instantaneous. Because some slow sorption occurred near saturation, the oxygen sorptive capacity of the copper could not be very accurately determined, but was taken arbitrarily as the total amount sorbed when an increment equal to about 2% of the previous sorption required as long as five minutes to drop to a pressure of 0.05 mm. After a reaction velocity run on the oxygen poisoned surface, reduction with hydrogen was carried out at 275° for one hour followed by evacuation at 225° for two hours. Following a run on an unpoisoned surface the temperature of reduction was 225.°

Indirect Poisoning with Oxygen.—Indirect poisoning was accomplished by three methods of selective reduction. Selective reduction (1), used for Cu XXI, comprised flushing the catalyst for one hour at 275° followed by evacuation for two hours at 225°; cooling to 0° in helium and sorbing an accurately measured amount of oxygen (15 cc. equal to about 85% saturation) from both ends of the catalyst bulb; adding a known increment of hydrogen (5 to 6 cc.); raising the temperature to 50° in the first half hour, to 75° in the second half hour, to 100° in the next hour (about 95% of the hydrogen had now disappeared), and finally to 125° for two hours in order to make the hydrogen disappear completely; closing off the catalyst and removing water from the trap (solid ammonia removed) then evacuating the catalyst for one half hour at 150°; then repeating the procedure with successive increments of hydrogen until a surface poisoned with the desired amount of oxygen remained; and finally evacuating for three hours at 160° prior to a reaction velocity run. The amount of oxygen poisoning was considered to be the difference between the amount of oxygen initially sorbed and the oxygen equivalent of the hydrogen admitted to the catalyst. A very small correction was necessitated for any traces of hydrogen not reacting. The most completely unpoisoned surfaces were prepared by flow reduction of sorbed oxygen for ten hours at 160° followed by evacuation for three hours at the same temperature.

Selective reduction (2), used for Cu XXII, differed from selective reduction (1) in that only 10 cc. of oxygen (67% saturation) were initially sorbed; in that the successive increments of hydrogen were somewhat smaller (3 to 4 cc.); and in that the time intervals were an half hour each at 25, 50, 75 and 100°. Probably due to the lower maximum temperature, about 5% of the hydrogen did not react under this treatment so that the oxygen remaining on the surface could not be as confidently calculated as before. Therefore, the amount of oxygen poisoning was determined also at the end of a velocity run by weighing the amount of water retained by a phosphorus pentoxide tube during the subsequent reduction at 275°. This "gravimetric" determination of oxygen poisoning has an advantage over the "buret" method in that it is direct, and it constitutes a valuable check on the latter method.

Selective reduction (3), used for Cu XXIII, differed from selective reduction (2) in that the reduction was prolonged for an additional hour at 100° and followed by an hour at 125°. The amount of oxygen poisoning was determined by the gravimetric method and also by the buret method since the hydrogen again reacted practically completely. The agreement of the two methods is apparent from experimental points shown on Curve 6, Fig. 2

Nitrous Oxide Poisoning.— Direct poisoning by nitrous oxide was accomplished by two methods. Nitrous oxide poisoning (1), used for Cu XXIV, comprised flushing the surface with hydrogen for five hours at 300° and evacuating for two hours at 375°; cooling to liquid ammonia temperature; admitting a measured amount of nitrous oxide; raising the temperature to 300° for one hour; and then cooling to 0°. The amount of oxygen poisoning was determined after the velocity run by the gravimetric method.

Nitrous oxide poisoning (2), used for Cu XXV, differed from nitrous oxide poisoning (1) in that the copper was flushed with hydrogen first at 275° for two hours, then at 225° for three hours and finally was evacuated for two hours at 225°. Furthermore, the nitrous oxide was heated only to 160°, which was the highest temperature to which sorbed oxygen was exposed in any of the selective reductions.

Experimental Results

A. Preliminary Work.—Although a number of copper catalysts both promoted and unpromoted, and in pulverulent and supported form were investigated, the granular copper[12] produced by the reduction of Kahlbaum cupric oxide proved to be the most active for the hydrogenation of ethylene at 0°. The reaction velocity-time curves obtained with all catalysts had a characteristic form when hydrogen was the gas to be displaced by the reaction mixture. During the first half hour the percentage conversion decreased at a diminishing rate and then remained constant, or at most showed a very gradual decrease with time (indicating that the scrubbing catalysts required regeneration). If ethylene were the gas displaced by the reaction mixture, the curve rose from a low initial conversion during the first half hour and then followed the course of the normal curve. It may be noted that the same type of curve was obtained for this reaction with a nickel catalyst down to −50°. Even with this metal when a steady state of conversion had been reached at 0° it was only necessary to displace temporarily the reacting gases with

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[12] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935).

hydrogen in order to cause a marked increase in conversion which, however, soon dropped back to the lower value. The initial period of diminishing catalytic activity in the velocity runs appears to be due to a rather slow removal of adsorbed hydrogen by interaction and displacement with ethylene in the establishment of a steady state. This same phenomenon has been found for this reaction using copper in static systems by others.[7,8]

Preliminary studies using copper poisoned with oxygen sorbed at 0° showed that while there was an extremely slow removal of sorbed oxygen at 20°, in the reaction velocity runs, no sorbed oxygen disappeared at 0°. This was particularly important to establish because former work[5] with thoria promoted, pulverulent copper indicated that some of the oxygen sorbed at 0° could, if not subsequently heated, react with hydrogen at this temperature. In the present work even a slow loss of sorbed oxygen, in the steady state, would have been indicated in the velocity runs by an ascending section in the velocity–time curve, and this never occurred at 0°. Furthermore, the amounts of oxygen found present at the end of the velocity runs agreed, within the experimental error, with the amounts of oxygen present before the runs.

It became apparent early in the present work that the catalyst surfaces were extremely sensitive to slight variations in their mode of production. For example when oxygen was sorbed at 0° and then removed by hydrogen at a lower temperature than that used in the production of the surface, marked activation occurred. However, subsequent evacuation of this surface at this lower temperature caused a considerable loss (sintering) in this activation. In order to ensure reliable and reproducible catalyst activity, therefore, all details of procedure were strictly standardized.

B. **Direct Oxygen Poisoning.**—The effects of different amounts of oxygen poisoning upon the activity of Cu XXI are shown graphically in Curve 5, Fig. 2. The oxygen was admitted to both ends of the catalyst bulb at 0°. Catalytic activity was determined here, and in all of the remainder of this work, by use of the ethylene-hydrogen reaction at 0° employing a one to one reaction mixture. The recorded catalyst activity refers always to the steady state. Oxygen appears to be a uniformly effective poison and a slight extrapolation of Curve 5 shows catalytic activity to disappear completely at 40% (6.3 cc. of oxygen sorbed) saturation of the surface with oxygen. The linear relation shown by Curve 5 would not be expected in view of the fact that the heats of oxygen sorption on copper decrease with increasing sorption,[5] unless the reaction were proceeding on uniform catalytic surface, or the oxygen poisoning were non-preferential. The latter possibility seemed the more probable.

C. **Heats of Oxygen Sorption.**—In order to gain information about the distribution of oxygen throughout the catalyst mass in the direct poisoning experiments, oxygen was now admitted to only the top or the bottom of the catalyst bulb. Such a procedure should make no difference in the successive values of the heat of sorption if the oxygen were uniformly distributed. The experimental results obtained on Cu XXI are shown graphically in Fig. 1. Curve 4 is taken from earlier work on copper (Cu 11)[5] for purposes of comparison and represents a case where the oxygen has been admitted to the catalyst bulb entirely from one end. Also, in the case of Curve 2 oxygen was admitted to Cu XXI entirely at the top of the bulb. The somewhat lower initial heats of sorption shown by Curve 2 may be attributed to the slightly lower temperature of outgassing used, while the still lower values shown on Curve 4 may be explained, in part perhaps, by the fact that Cu 11 was in pulverulent rather than in granular form. It is at once apparent from a comparison of the smooth Curves 2 and 4 with Curves 1 and 3, that the different method of

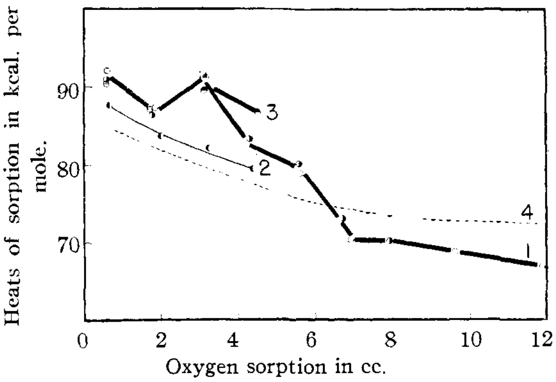

Fig. 1.—Heats of oxygen sorption on copper. Symbols indicate to which end of catalyst oxygen was admitted. Curve 1: ◑ bottom, ⦶ top, Run 138, Cu XXI; ○ top, ⍥ bottom, Run 139, Cu XXI. Curve 2: ◐ top, Run 143, Cu XXI. Curve 3: ⊖ top, ◓ bottom, Run 144, Cu XXI. Curve 4: top, earlier work on Cu 11.

admitting oxygen employed for the latter curves has been responsible for the introduction of maxima and minima. In the case of the composite Curve 1 all of the oxygen except the third increment was admitted to the same end of the catalyst bulb. Curve 3 differs in that both the third and fourth (last) increments were admitted to the same end.

The interpretation of these curves seems fairly clear if, when an increment of oxygen is admitted to one end of a cylindrical copper catalyst, it is assumed that although the gas is pretty largely sorbed upon the first portions of the catalyst encountered, yet some preferential sorption occurs and a sorption gradient is set up in which the concentration is greatest on those parts of the catalyst surface first contacting the oncoming oxygen molecules. A larger and larger part of each successive increment of oxygen admitted to the given end will be sorbed upon previously, partially saturated surface with the observed decrease in the heats of sorption, which can be neither strictly integral nor differential values. A comparison of the fourth points on Curves 1 and 3 indicates the additional decrease in heat of sorption which an increment of oxygen suffered when it had to encounter surface which had been partially saturated by two, rather than one earlier increment of oxygen. When in addition to traversing surface partially saturated by earlier increments from the same end, an increment of oxygen meets surface saturated in part by oxygen admitted to the other catalyst end, an abnormally large decrease in heat of sorption would be anticipated. With Curve 1 it is clear that the third increments of oxygen were sorbed upon surface entirely unreached by the first and second increments admitted from the other end. It was not until five increments were admitted from one end, that the drop in this curve indicates that oxygen had penetrated to surface which sorbed the single increment admitted to the other end. When increments of oxygen were added alternately to the two ends of the granular copper catalyst, a curve (not shown) was obtained which showed a sharp drop at roughly 70 k. cal. and about 5 cc. of oxygen sorbed. From a slight extrapolation of Curve 5, Fig. 2, it is clear that when oxygen was admitted to both ends simultaneously, no more than 6.3 cc. was necessary for complete penetration of the catalyst. From the foregoing it appears that from 5 to 6 cc. of oxygen was required in the direct oxygen poisoning experiments before all parts of the catalytically active surface of the granular catalyst came into contact with any oxygen. Thus as far as surface capable of catalyzing the ethylene–hydrogen reaction is concerned, the direct sorption of oxygen proves to be largely, if not entirely, non-preferential. Therefore, no significant correlation can be expected between catalytic activity and either extent of direct oxygen poisoning, or heats of sorption, and the linear relation shown in Curve 5, Fig. 2, need give no true picture of the catalyst surface.

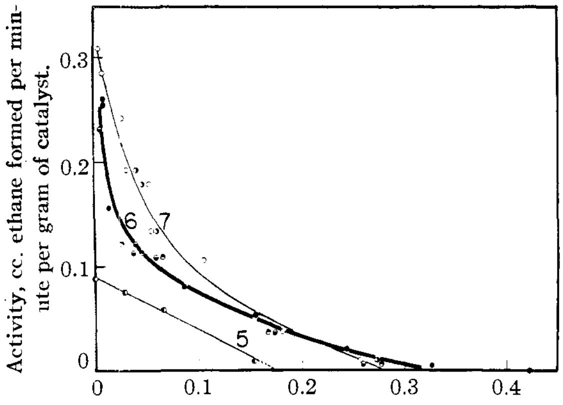

Fig. 2.—Direct and indirect oxygen poisoning. Direct poisoning: Curve 5, Runs 131–137 on Cu XXI at gas flow (cc. per min.) of H_2 = 5.9 and C_2H_4 = 5.6.

Indirect poisoning by means of selective reductions (S. R.): Curve 6, S. R. (1), ● "buret" method, Runs 153–161 on Cu XXI at gas flow of H_2 = 11.6 and C_2H_4 = 11.2; S. R. (3), ◓ "buret" method, ◒ "gravimetric" method, Runs 180–185 on Cu XXIII at gas flow of H_2 = 5.9 and C_2H_4 = 5.6. Curve 7, S.R. (2), ◑ "buret" method, ○ "gravimetric" method, Runs 166–174 on Cu XXII at a gas flow of H_2 = 11.6 and C_2H_4 = 11.2.

D. Indirect Oxygen Poisoning.—Inasmuch as it was clear from the work already done that a preferential poisoning of copper had not been achieved, it was decided to investigate the possibility of a selective removal of oxygen from a previously poisoned surface. Curves 6 and 7, Fig. 2, relate catalytic activity and various amounts of oxygen poisoning produced by the successive removal of larger and larger portions of previously sorbed oxygen by means of the careful, low-temperature reductions with measured amounts of hydrogen, described in detail under Experimental Method. Curve 7 was obtained with Cu XXII, which was Cu XXI after it had been accidentally activated, and thus its major portion lies above Curve 6. Because of the experimental arrangements, the hydrogenation of ethylene on the nearly unpoisoned surface of Cu XXII was now close to 100%. The two uppermost points on Curve 7 are, therefore, somewhat too low and thus displace the curve too far to the left. The various symbols employed on Curves 6 and 7 indicate the experimental method used in determining the amount of oxygen poisoning. The "buret" and "gravimetric" methods agree within their experimental errors. The lowest points on Curves 6 and 7, which were obtained after heating the sorbed oxygen to 160° for three hours and prior to any reduction, indicate that 15 cc. of oxygen poisoned Cu XXI completely while Cu XXII and XXIII showed a slight activity for 10 and 5.5 cc. of oxygen, respectively. Comparison of Curves 5 and 6 indicates that about twice as much oxygen was required completely to poison Cu XXI in the latter case. This decrease in the poisoning efficiency of oxygen may be attributed to a partial "regeneration" of the poisoned copper by the heating at 160°, a phenomenon encountered in earlier work.[5]

Inasmuch as not quite all of the oxygen poisoning could be removed even by very prolonged flow reduction at 160°, no experimental values could be obtained for completely unpoisoned surfaces. Complete removal of sorbed oxygen could be effected at 275° but this caused the loss in activity apparent from a comparison of the ordinates of the highest portions of Curves 5 and 6. The phenomenon of activating copper by alternate oxidation and reduction at successively lower temperatures is well known, and it now appears that oxygen sorption at 0° followed by reduction at 160° produced a more active surface than when reduction occurred at 275°, and when reduction was carried out at 90° about twice the activation noted above in Fig. 2 occurred. Furthermore, the activities of these surfaces were strictly reproducible. It is suggested that the activations in the present work are associated with a displacement of surface copper atoms during the highly exothermic oxygen sorption. It appears, therefore, that the surface uncovered in the selective reductions was not exactly the same surface which was previously poisoned, and it is not known whether the former would be more or less active than that produced by a similar reduction of normal copper oxide. Although the Cu XXI of Curve 6 is not quite the Cu XXI of Curve 5, it is believed that the two surfaces are not unrelated. The general form of Curves 6 and 7 shows that the removal of sorbed oxygen was accompanied by an exponential increase in the catalyst activity. It appears, therefore, that various portions of the sorbed oxygen differed in ease of reducibility. It is believed that this is to be attributed to the presence of different surface types on the copper upon which sorption occurred. It is felt that in the successive selective reductions the factor for regeneration was kept constant, and also that appreciable penetration of sorbed oxygen below the available surface of the catalyst was unlikely because the copper was only partially saturated with strongly held oxygen at 0° and became much less saturated at higher temperatures, and furthermore were the oxygen last removed, in the successive reductions, from the interior of the catalyst, it would seem necessary to associate the greatest catalyst activity with this location. It seems reasonable to conclude, therefore, that the successive reductions were selective in that surface less active in the ethylene–hydrogen reaction was released first and increasingly more active surface thereafter.

E. Nitrous Oxide Poisoning.—Because of the desirability of finding a direct method for poisoning copper it was decided to investigate the possibilities of decomposing nitrous oxide at the catalyst surface. Preliminary studies with a catalyst similar to Cu XXI at temperatures up to 75° indicated that decomposition occurred with no increase in pressure and that, therefore, most probably one atom of oxygen was sorbed for each molecule of nitrogen liberated. This mechanism, which also occurs in the case of silver,[13] was supported by later work with Cu XXIV and XXV. The preliminary studies also indicated that a portion of the nitrous oxide was decomposed probably instantaneously at −78°, and after sintering the copper at 400° some still decomposed similarly at −45°. In an endeavor to make the poisoning as selective as possible, Cu XXIII was now sintered at 400° thereby producing Cu XXIV, and the nitrous oxide was in all cases admitted at about −40°. To ensure more complete decomposition and a strong sorption of oxygen the temperature was then raised to 300° for Cu XXIV and to 160° for Cu XXV.

The effects of various amounts of poisoning

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[13] A. F. Benton and C. M. Thacker, THIS JOURNAL, **56**, 1300 (1934).

from nitrous oxide upon the catalytic activity of Cu XXIV are shown in Curve 8, Fig. 3. The considerable horizontal portion of this curve indicates that some 3.5 cc. of oxygen was taken up by the catalyst before its capacity for hydrogenating ethylene under the experimental conditions was diminished. Curve 8 falls fairly rapidly once poisoning starts but its form is obviously uncertain in the vicinity of the last point. Even though relatively large excesses of nitrous oxide were employed more complete poisoning was not achieved.

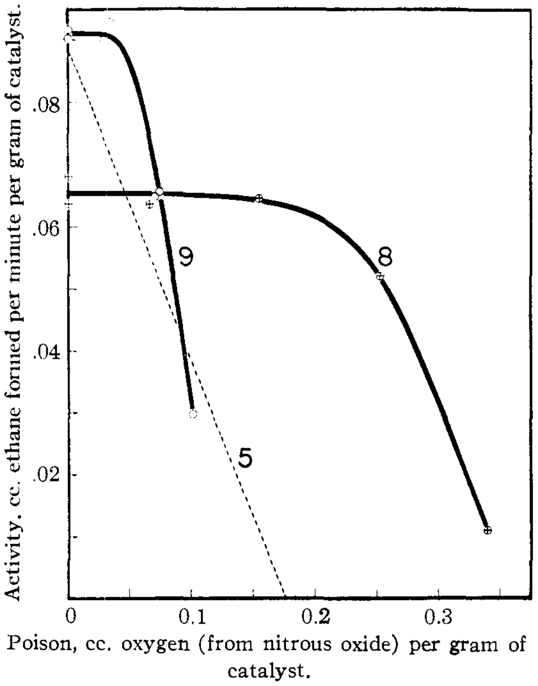

Fig. 3.—Nitrous oxide poisoning. Gas flow (cc. per min.): H_2 = 4.6; C_2H_4 = 4.5; Curve 8: nitrous oxide poisoning (1); Runs 190–195, Cu XXIV. Curve 9: nitrous oxide poisoning (2); Runs 204–211, Cu XXV. (Curve 5: direct oxygen poisoning (Fig. 2).)

Curve 9, Fig. 3, shows the effects of poisoning Cu XXV with nitrous oxide at the lower maximum temperature of 160°. In a comparison of unpoisoned surfaces the relative position of Curve 5 in Figs. 3 and 2 clearly shows the absence on Cu XXV of the activation characteristic of the indirect poisoning (Curve 6). While the displacement of Curve 9, Fig. 3, above Curve 8 is to be attributed to the greater activity of Cu XXV, the considerable lateral displacement of the former curve toward the left must be due, for the most part, to the increased efficiency of the nitrous oxide when decomposed at the lower temperature of 160°. Although the horizontal portion of Curve 9 is much shorter, it should be noted that it still proves to be roughly the same fraction of the total abscissa of its curve, so that its relative length is little changed. At all points except the last on Curve 9 decomposition was considered complete, in that the amount of oxygen poisoning found by the "gravimetric" method after a velocity run agreed with the oxygen present in the charge of nitrous oxide admitted. Since at the last point on Curve 9 nitrous oxide decomposition was incomplete at 160°, this curve was not extended farther and no extrapolation appears justified on the basis of the present experimental evidence. Since an excess of nitrous oxide was present at the last points on both Curve 8 and 9, it appears that the surfaces were completely poisoned for further nitrous oxide decomposition at the temperatures employed. It seems important to note, however, that the remaining unpoisoned surface was still active enough to catalyze the hydrogenation of ethylene at 0°. From this it appears that more active surface is required for nitrous oxide decomposition than is required for the ethylene–hydrogen reaction, although there must be some overlapping as is evident from the fact that nitrous oxide acts as a poison at all for the latter reaction. Further evidence for the selective nature of the nitrous oxide poisoning rests upon the interpretation of the horizontal portions of Curves 8 and 9. While regeneration must be a considerable factor at 300°, it becomes smaller at 160°, and one experiment gave qualitative evidence that the horizontal portion is present when the maximum temperature of nitrous oxide decomposition was 25°. Inasmuch as the decomposition of nitrous oxide is a surface reaction, it appears hardly probable that the horizontal portions of the curves resulted from the diffusion of all the oxygen into the catalyst interior leaving the surface bare. It seems reasonable, therefore, to assume that the nitrous oxide poisoning was selective in nature.

Discussion

Evaluation of the curve obtained in the direct oxygen poisoning experiments, in the light of the work on heats of oxygen sorption, clearly shows that this curve need not constitute a true picture of the catalytic surface of copper. Thus caution must be employed in the interpretation of experiments involving strongly sorbed poisons. Only if the poison is capable of being preferentially or selectively sorbed (portions of a non-uniform surface are progressively poisoned in the order of their relative activities) will a linear relation between activity and extent of poisoning constitute proof for a uniform surface.

All of the evidence in the present work may be considered support for a non-uniform copper surface. Thus (a) the direct oxygen poisoning experiments reveal that a large fraction of the surface was catalytically inactive, (b) the heats of oxygen sorption diminished as sorption increased, (c) the indirect oxygen poisoning experiments released a surface having portions of widely different hydrogenating capacities, and (d) the nitrous oxide poisoning experiments also appear to require the existence of a surface which is non-uniform in catalytic activity.

The experimental work furnishes evidence that the ethylene–hydrogen reaction at 0° proceeded on a portion of the catalyst surface having intermediate activity. Thus a slight extrapolation of the linear curve obtained in the direct oxygen poisoning experiments indicates that about 60% of the surface, which sorbed oxygen strongly, possessed no catalytic activity for the reaction studied. This does not mean, however, that all of the remaining 40% of the surface was catalytically active. In fact the non-selective nature of the direct oxygen sorption makes this unnecessary and, furthermore, the initial horizontal portions of the curves for nitrous oxide poisoning (Curves 8 and 9, Fig. 3) appear to constitute direct evidence that some of the copper surface was too active to contribute to the catalysis of the hydrogenation of ethylene. This too active surface, which preferentially decomposed nitrous oxide, may well be wholly or in part that which is inhibited by the known strong sorption of ethylene during the hydrogenation reaction at 0°.[14] At higher temperatures, due to desorption of ethylene, this "too active" surface may actively participate in the catalysis.

Taken together, Curves 6 to 9 (Figs. 2 and 3) constitute evidence as to the nature of the catalyst surface upon which the low-temperature hydrogenation of ethylene proceeded. It is highly improbable that the removal of sorbed oxygen by the selective reductions was entirely preferential. Also regeneration appears to have decreased the poisoning efficiency of the oxygen. A correction for both of these factors should have the effect of diminishing the horizontal length of Curve 6, while causing the curve to rise even more slowly in the region of large amounts of poisoning, and still more rapidly for the smaller amounts. The possibility that such a curve might bend sharply from the rapidly rising portion to a nearly horizontal portion, similar to that found experimentally in Curve 9, is not excluded. In fact, this might be expected if in the selective reductions none but the most active surface were released at the end. In the present work the general form of Curve 6 appears to constitute the best experimental evidence for the nature of the surface capable of catalyzing the hydrogenation of ethylene under the experimental conditions, and is consistent with an exponential distribution of reaction centers such as has been postulated by Constable on copper,[15] the bulk of the reaction occurring on relatively few centers of low activation energy. However, as has been noted above, these most active centers for the hydrogenation of ethylene appear not to be those centers most active in the decomposition of nitrous oxide.

Because of the different schools of thought concerning the structure and behavior of catalyst surfaces, the experimental details of this work have been rather fully presented in order to afford adequate basis for independent interpretation. While the foregoing interpretation appears to us simple and in accord with the present evidence, it is realized that more evidence is highly desirable and, therefore, further work is being undertaken with this end in view.

Summary

1. Active, granular, copper catalysts have been poisoned to various degrees with oxygen both directly and indirectly, and with nitrous oxide. The catalytic activity of both poisoned and unpoisoned surfaces has been measured by means of the ethylene–hydrogen reaction at 0° using a flow method.

2. As the amount of oxygen directly sorbed by the copper at 0° was increased, both the heats of oxygen sorption and the catalytic activity of the surface decreased, the latter in a linear manner.

3. By means of suitable heat of oxygen sorption measurements it was shown that active copper sorbed oxygen at 0° in an almost non-

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[14] R. N. Pease, THIS JOURNAL, **45**, 1196 (1923).

[15] F. H. Constable, *Proc. Roy. Soc.* (London), **108**, 355 (1925).

selective manner and, therefore, that the linear relation in 2 need give no true concept of the catalyst surface.

4. An indirect method of poisoning active copper with oxygen appears to be selective in character.

5. Direct poisoning of active copper with nitrous oxide also appears to be selective.

6. All of the experimental evidence is considered to indicate (a) that the copper surface is non-uniform and (b) that at 0° the hydrogenation of ethylene proceeds almost exclusively on a relatively few surface types, probably of intermediate character.

7. The interpretation of the experimental evidence is consistent with an exponential distribution of centers active at 0° in catalyzing the ethylene–hydrogen reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

A Study of the Dehydration of Hydrated Cobaltic Oxide

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The literature[1,2,3,4] gives various temperatures, ranging from about 150 to 385°, at which hydrated cobaltic oxide begins to decompose into Co_3O_4, oxygen and water. The observations made in this Laboratory indicate the reason for the apparent disagreement of the investigators.

Experimental

Various lots of hydrated cobaltic oxide were prepared by alkaline decomposition of chloropentammino-cobalti chloride, as recommended by Hüttig and Kassler[1] except that the colloidal oxide was isolated by centrifuging instead of using a membrane filter. The oxide was then dried two days over concentrated sulfuric acid in a vacuum desiccator and ground in an agate mortar. Analyses of the partially dehydrated oxides showed the practical absence of divalent cobalt, and a water content corresponding to about $Co_2O_3 \cdot 1.6H_2O$, or a calculated value of about 15% water and 85% of the hypothetical anhydrous Co_2O_3. The oxide thus prepared was then dehydrated at various temperatures. This was done by passing highly purified air over the oxide samples while the latter were constantly agitated with a mechanical shaker to provide uniform conditions. The approximate progress of the dehydration was determined at twelve or twenty-four-hour intervals by weighing the amount of water collected in dehydrite absorption tubes connected to the air exhaust. Each run was continued until the loss of water decreased to about 0.5 mg. in twenty-four hours. This usually required from two to four days. The oxide was then analyzed for trivalent cobalt by the oxalate–permanganate method as recommended by LeBlanc and Möbius[5] and for water by heating the oxide to red heat in a combustion furnace, using a dehydrite absorption tube to collect the water.

TABLE I

RESULTS OF EXPERIMENTS

Temp., °C., ±3°	% Co_2O_3[a] remaining	% H_2O remaining	% H_2O, calcd. for $Co_2O_3 \cdot 1H_2O$
155	35.3	4.6	3.83
168	19.0	3.8	2.06
177	17.3	2.7	1.88
195	13.3	3.1	1.44
205	19.3	2.3	2.09
220	9.7	1.5	1.05
235	10.3	1.4	1.12
260	15.7	2.2	1.70

[a] Hypothetical anhydrous oxide.

It was noticed in all cases that the rate of dehydration is very slow up to 90°, but in the range from 100 to 180° rapid dehydration takes place. For example, a 1.5-g. sample heated for twenty-four hours at 105° lost 0.006 g.; during the next forty-eight hours at 180° it lost an additional 0.163 g.; then during the next eighty-four hours at 250°, only 0.003 g. additional. In some cases, however, the dehydration at the end of 200° treatment was not nearly as complete as shown above for 180°, and a considerable amount of water continued to be evolved at still higher temperatures.

Further information was obtained in attempts to prepare anhydrous Co_2O_3 by oxidation with

(1) G. Hüttig and R. Kassler, *Z. anorg. Chem.*, **184**, 283 (1929).

(2) G. Natta and M. Strada, *Gazz. chim. ital.*, **58**, 428 (1928).

(3) F. Merck and E. Wedekind, *Z. anorg. allgem. Chem.*, **186**, 68 (1930).

(4) T. Carnelley and J. Walker, *J. Chem. Soc.*, **53**, 90 (1888).

(5) M. LeBlanc and E. Möbius, *Z. physik. Chem.*, **142**, 170 (1929).