the complete reduction of ammonium ion to hydrogen, silver (I) iodide to silver, and bismuth(III) iodide to bismuth.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

The Catalytic Reaction of Hydrogen and Oxygen on Plane Faces of a Single Crystal of Copper[1]

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Introduction

The determination of the positions of different activity on a catalyst surface is a question of primary importance. The two great difficulties in determining these positions are the preparation of a surface of known structure and the development of a method for following changes in the structure as the reaction takes place.

Most studies made in the past on the activity of a solid catalyst surface have consisted of measuring the amounts of materials consumed and produced by powdered metal catalysts. Such catalysts generally consist of many crystals randomly arranged and exposing faces, edges and corners of many kinds. Measurements made on such materials are composite quantities and give little direct information about the reactivity of the various types of structure exposed.

In an effort to obtain simple, reproducible surfaces of known structure, large single crystals with surfaces prepared parallel to special planes were selected. Furthermore, previous studies with large single crystals[2] have shown that the rate of many surface processes varies with the crystal face exposed at the surface. Therefore in order to determine the influence of crystal plane on catalytic activity and to extend our knowledge of metal surfaces in general, studies have been made of the reaction of hydrogen and oxygen on several plane faces of a large single crystal of copper.

In the study of the reaction of gases on the surface of metallic crystals, it has been found that the reactions may be divided into two classes, those which readily produce rearrangements in the surface and those which do not, at least on a microscopic scale. The reaction of hydrogen and oxygen on copper belongs to the first class. The nature of the rearrangements produced by the action of hydrogen and oxygen will first be described, and then the measurement of rates on several faces will be presented. An important feature of these studies is the correlation between catalytic activity and surface structure which can be observed.

Method of Experiment

Preparation of Surface of Catalyst.—There is a tendency in catalytic studies to underrate the importance of the preparation of the surface. Very fine measurements are often of limited value because they are made on surfaces, about the structure and composition of which little is known. Emphasis was placed in these studies on the preparation of the surface.

Single crystals of copper in the form of rods, $^5/_8$ in. in diameter and 4 in. long, were grown by the method previously described.[2,3] For use in the studies of rearrangements, spheres were machined from the $^5/_8$ in. rods and polished mechanically and electrolytically. For the rate measurements thin slices, about $^1/_8$ in. thick and parallel to the (100) and (111) planes were cut from a 1-inch crystal. In order to assure that there could be no difference in the chemical composition of the two crystal faces on which rates were measured, a sphere was machined from a 1-inch rod, and two flat faces, one parallel to the (100) face and one to the (111) face, were cut on the sphere. This was done by the same method used in cutting the slices. Photographs of the several specimens are shown in Figs. 2 and 14. The flat faces for rate measurements were polished as follows. The face was mechanically polished with metallographic polishing papers nos. 1 through 0000, and after each paper it was electrolytically etched in the polishing solution at a current density of about 0.02 amp./sq. cm. for a sufficient length of time to remove the strained layer produced by the last mechanical polishing. The time varied from about thirty minutes after the no. 1 paper to about ten minutes after the last paper. After the last etching the surface was slightly roughened on a microscopic scale but plane on a macroscopic scale and in a strain-free condition. The final step consisted of polishing mechanically on a felt wheel moistened with levigated alumina. In order to prevent subsequent recrystallization of the surface it was necessary to keep the cloth wet, to operate the wheel at a slow speed of about 150 r.p.m., and to press the specimen only lightly against the felt. After the first treatment with the reacting gases, it was only necessary to repolish with the 0000 paper and alumina, or with alumina alone. The surface was swabbed with a soft tissue under a stream of water in order to remove traces of alumina. Surfaces prepared by this method gave essentially the same results as those prepared by careful electrolytic polishing but the method described above was generally used because of the tendency of large surfaces to become pitted during electrolytic polishing. In order to reduce oxide and remove any distortion in the surface, all crystals were annealed in hydrogen at 550° for at least sixteen hours immediately prior to study of rearrangements or measurement of rates of reaction.

The Study of Rearrangements.—Since the surface of a monocrystalline sphere of copper exposes every crystal plane in at least six places, the (100) face appearing six times, most of the rearrangement studies were carried out on $^5/_8$ in. spheres. Also the symmetry of the patterns on a sphere make it easy to identify the location of the crystal faces. For the study of rearrangements the sphere was supported, generally with shaft downward, within the bulb of a glass apparatus connected with suitable inlet and exit tubes. The sphere was placed in the apparatus through a ground glass joint at the top and was suspended from the upper half of the joint by means of a no. 20 B. and S.

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[1] This work was supported by a grant from the Research Corporation.

[2] See Leidheiser and Gwathmey, *Trans. Electrochem. Soc.*, **91**, (1947) [printed as Preprint 91-6, but not yet published] for a résumé of previous studies with massive single crystals.

[3] Gwathmey and Benton, *J. Phys. Chem.*, **44**, 35 (1940).

gage copper wire. When it was desired to protect the supporting wire from the action of the gases in order to prevent a change in concentration of the gases before they reached the crystal, the wire was enclosed in a glass tube and the shaft of the sphere, pointing upward, was inserted into the lower end of the tube. The appearance of the crystal as the reaction proceeded was observed through a glass window in the side of the furnace, the inside of which was illuminated by a small light at the top. Different crystal faces could be brought into view opposite the window by rotating the upper half of the ground glass joint to which the supporting wire was attached. It was found convenient, in identifying crystal regions during the early states of formation of the pattern, to have three adjacent (100) pole positions previously marked on the sphere by means of a deep pin prick. One great advantage of this method of study is that it is possible to follow changes in surface structure as the reaction proceeds.

The crystals were finally removed from the reaction chamber and examined under a microscope and in a darkened room with the aid of a flashlight. The methods of examining the patterns, identifying the planes and recording the results have been previously described.[2] The temperature of the reaction was assumed to be the temperature of the air just outside of the reaction vessel as measured by a mercury thermometer. The question of the exact temperature of the catalytic surface will be discussed later. In all reactions with the spheres the rate of flow of gas approximated 200 ml./minute.

Measurement of Rates of Reaction.—In order to determine rates on a surface prepared parallel to one particular crystal plane, it is necessary to prevent from exposure to the reacting gases other parts of the crystal, such as other faces, edges, and corners. Several different methods of accomplishing this were tried, but the simple apparatus shown in Fig. 1 was found to be satisfactory for the reaction under consideration. The surface of the crystal was ground flat and placed on top of the enclosed tube A, which had been flanged on the upper end and likewise ground exceedingly smooth. The crystal was placed in position and the outer glass cover tube was vacuum sealed to the base of the apparatus with the aid of a ground glass joint. The incoming gases consisting of purified tank hydrogen and electrolytic oxygen passed up the center tube, reacted on the surface of the crystal, passed down the middle tube, and out through a drying train of calcium chloride and Dehydrite where the water formed was absorbed. The rate of flow of the gases was measured with the aid of orifice meters and was 40 ml./min. unless stated otherwise. A furnace was placed over the top of the apparatus and extended down to within about 6 in. of the upper ground glass joint. The temperature was kept constant in the final experiments by means of a thermoregulator. In the experiments with thin slices an iron weight sealed in glass was placed on the slice to hold it in place. In experiments with the spheres on which the two faces had been cut, this was unnecessary. The failure of the polished surface to rearrange in the region of the crystal not exposed to the action of the flowing gases indicated that the amount of gas which leaked by the metal-flange joint was negligible. A photograph showing the difference in the appearance of the region exposed to the direct action of the gas and that of the region in the dead space surrounding the inner reaction chamber is given in Fig. 2. The apparent surface of the metal exposed to the action of the gases was always 2.69 sq. cm. Through the aid of this apparatus it is possible to measure the rates of reaction on surfaces prepared parallel to special crystal planes and containing always the same apparent area. At the completion of a run the surface of the crystal was examined under the microscope and in a darkened room with the aid of a flashlight. During preliminary studies, whenever inconsistent rate measurements were obtained because of such reasons as recrystallization of the surface or the presence of an accidental impurity, it was found that the final appearance of the surface was always abnormal.

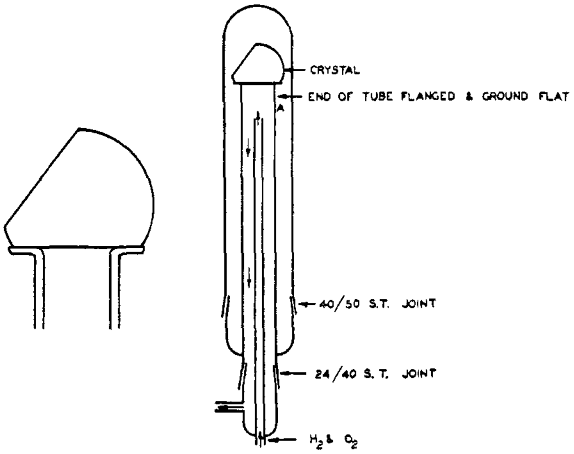


Fig. 1.—Apparatus for measuring rate of catalytic reaction of hydrogen and oxygen on plane faces of a metallic single crystal.

Results

Rearrangements of the Surface.—Rearrangements of the metallic surface under the action of reacting gases have been found to take place with a number of metals and gases. The nature and the intensity of the rearrangement depend on the metal, the gases, and the conditions of the experiment such as temperature and gas flow. Only rearrangements produced by the action of hydrogen and oxygen on copper will be described, although a photograph of the hydrogen–oxygen reaction on nickel is shown in Fig. 3 to illustrate the complicated fine structure of a pattern produced by another system. Brief mention has previously been made that such rearrangements take place on the surface of a copper crystal serving as a catalyst for the reaction of hydrogen and oxygen.[4]

Experiments were carried out over a temperature range of 360–440° and an oxygen concentration of 1–20%. The rearrangements which took place with 14% oxygen at a temperature of 400° will be described. Within a few seconds after oxygen was added to the stream of hydrogen in which the crystal was being heated, the surface of the crystal became slightly foggy in certain preferred crystal regions. After about fifteen minutes a definite pattern of light reflections from certain regions could be seen when a beam of light was directed through the window in the furnace wall, and after sixteen hours the striking pattern shown in Figs. 4 and 5 was obtained. Photomicrographs of the final surface structures on several different faces are shown in Figs. 6–10. The surface immediately at the (111) face remained quite smooth, while that at the (100) became very rough. Still another type of structure developed at the (110). Not only did the (111) face remain relatively smooth but (111) planes developed in large three-armed areas adjacent to each (111) pole as shown by the photograph in Fig. 5 taken when a beam of

[4] Gwathmey and Benton, *J. Chem. Phys.*, **8**, 569 (1940).

light was directed normally to the surface at the (111) pole. (110) planes were slightly developed in the (100) regions as shown by faint reflections obtained from these regions when a light beam was directed normally to the surface at the (110) pole. The facets developed parallel to these special planes as described above could also be identified by examination under the microscope. Figure 11 shows a microscopic view of a polycrystalline surface exposed to a hydrogen–oxygen mixture at 400°. Structures characteristic of the various surface regions on a monocrystalline sphere may be observed on the individual grains. The specimen shown in Fig. 11 was formed by recrystallization of a single crystal, although similar surface structures have been observed on many polycrystalline samples of copper.

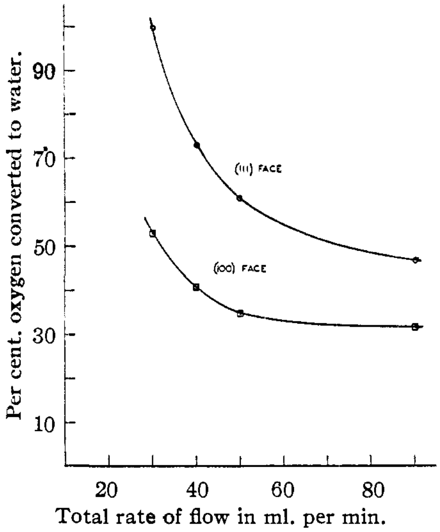


Fig. 12.—Curves showing change in rate of reaction with change in rate of flow: 400°, oxygen flow = 0.5 ml. per min., hydrogen flow varied.

Although many features of the patterns were the same over a temperature range of 360–440° and an oxygen concentration of 1–20%, there were some variations depending on the oxygen concentration and the time of reaction. With an oxygen concentration of 14% after sixteen hours, (111) planes were developed in large areas surrounding the (111) poles, but after about twenty-four days the development of (111) planes had decreased and (110) planes had developed in large areas surrounding the (110) poles. After seven days at this concentration a reddish-brown powder had formed over the entire surface. When this powder was wiped off with a tissue at the end of twenty-four days, the typical pattern with the exception noted above was observed. When the powder was removed, the contrast between the smooth (111) and the rough (100) areas was not as striking as it had been before the powder formed. The formation of this powder appears to be similar to the disintegration of copper tubes by heating in ammonia as observed by Beilby and Henderson.[5]

The presence of a small amount of a second metal, such as zinc or nickel, when electrodeposited on a copper sphere greatly influenced the pattern formed by the catalytic reaction of hydrogen and oxygen.

Measurement of Rates of Reaction.—Since the rate of reaction depends on the type and total area of surface exposed as a result of rearrangement, it is essential that the nature of the surface be known to some degree of approximation when the rates of reaction are measured. The change in the nature of the surface with the conditions of the experiment makes it difficult to present a complete picture of all events taking place in this reaction. A detailed study of each individual surface might reveal much additional information about its structure, but in the studies herein reported the structure was examined by the methods described, primarily for the purpose of showing the differences in structure of the various faces and the influence of these differences on the rates of the catalytic reaction.

No powder was ever observed on either face over a period of seven days with an oxygen concentration of 1.25% or less. Therefore experiments carried out within this range should give results which are dependent on the rearranged structure of the individual faces and are independent of the influence of the powder which forms at higher oxygen concentrations. As will be shown later, when a large amount of copper powder forms on the surface, the specific influence of the crystal face will be obscured.

With oxygen concentrations in the range of 0.6–2.5% and temperatures from 250–420°, the rate of reaction on the (111) face was approximately twice that on the (100) face, although the latter face had become much rougher and therefore exposed more surface area than the (111) face. All rates of reaction for both faces are referred to the same amount of apparent starting surface, 2.69 sq. cm. A plot of the rates of reaction on the (111) and (100) faces for various rates of flow of the reacting gases is shown in Fig. 12. The variations in the rates of reaction with temperature are shown in Fig. 13. The difference in the roughness of the (100) and (111) faces after reaction had taken place is shown in Fig. 14. The photograph was taken looking down on the sphere with the flat (100) face on the left side of the sphere and the (111) face on the right side, both faces making the same angle with the plane of the photograph. The crystal was illuminated from both sides, the beams of light pointing down and making an angle of about 45° with the plane of the photograph. The part of the (100) face on which the reaction took place appears as the light elliptical-shaped region in the center of the face on the left since the light was scattered upward by the rough surface. The part of the (111) face on which reaction took

(5) Beilby and Henderson, *J. Chem. Soc.*, **79**, 1245 (1901).

Fig. 2.—Typical appearance of a (100) slice exposed to a mixture of hydrogen and oxygen at 400° for forty-eight hours.

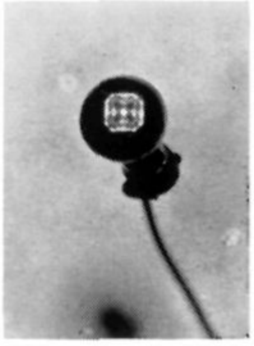


Fig. 3.—Action of a 7:1 mixture of hydrogen and oxygen on a nickel single crystal at 420° for three days. Normal to (100).

Fig. 4.—Action of a 7:1 mixture of hydrogen and oxygen on a copper single crystal at 400° for sixteen hours. Normal to (100). Four bright lights were focused on (110) areas.

Fig. 5.—Action of a 7:1 mixture of hydrogen and oxygen on a copper single crystal at 400° for sixteen hours. Normal to (111). Note strong reflection from area around (111) pole.

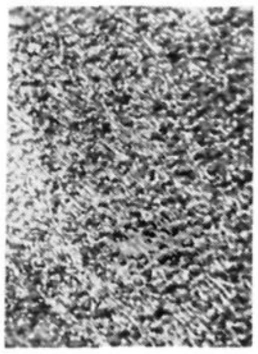


Fig. 6.—Action of a 7:1 mixture of hydrogen and oxygen on a copper single crystal at 400° for sixteen hours: at (100), ×600.

Fig. 7.—Action of a 7:1 mixture of hydrogen and oxygen on a copper single crystal at 400° for sixteen hours: at (111), ×600.

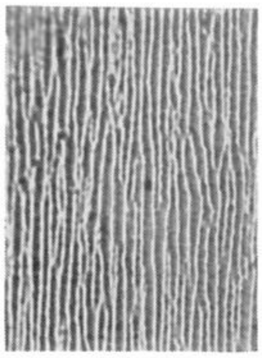


Fig. 8.—Action of a 7:1 mixture of hydrogen and oxygen on a copper single crystal at 400° for sixteen hours: at (110), ×600.

Fig. 9.—Action of a 7:1 mixture of hydrogen and oxygen on a copper single crystal at 400° for sixteen hours: near (100), ×600.

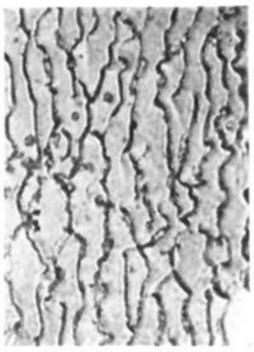


Fig. 10.—Action of a 7:1 mixture of hydrogen and oxygen on a copper single crystal at 400° for sixteen hours: near (111), ×600.

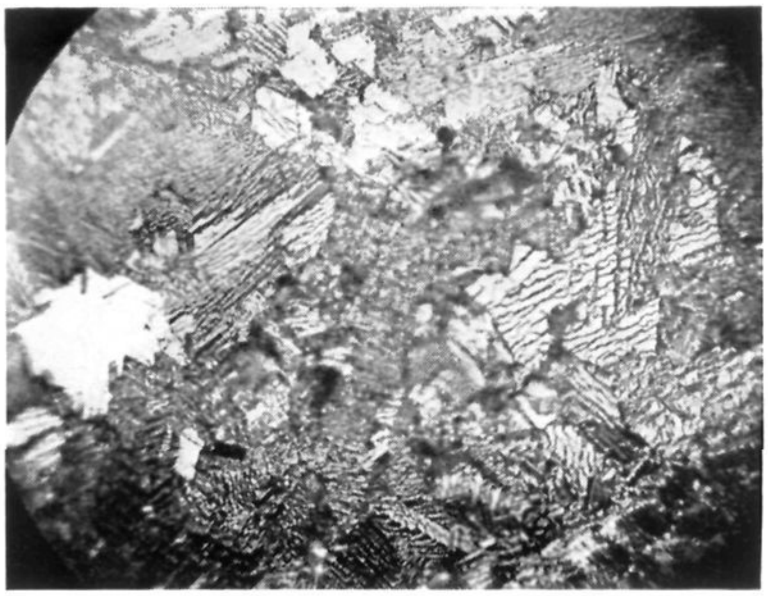


Fig. 11.—Polycrystalline copper surface exposed to a hydrogen–oxygen mixture at 400°, ×200, compare with Figs. 6–10.

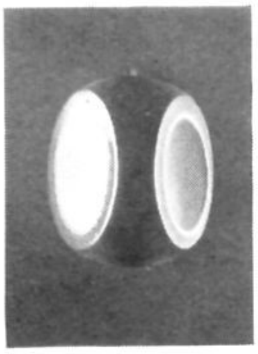


Fig. 14.—Photograph showing difference in roughness of (100) and (111) faces after independent exposure to a hydrogen–oxygen mixture containing 1.25% oxygen at 400° for forty-eight hours. (100) face on left, (111) face on right.

Fig. 15.—Microscopic view of (100) face shown in Fig. 14, ×650.

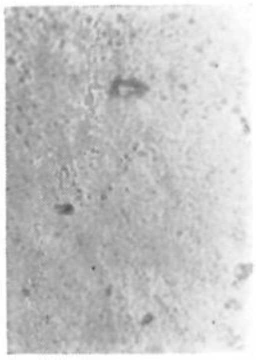


Fig. 16.—Microscopic view of (111) face shown in Fig. 14, ×650.

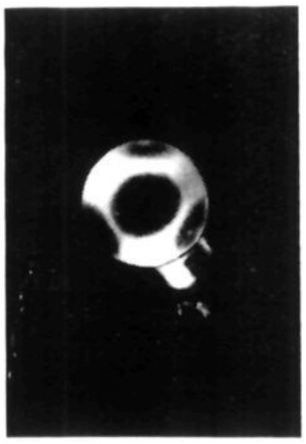


Fig. 1.—Selective deposition of carbon on the (111) face of a nickel crystal heated at 550° in carbon monoxide; view normal to (111) (see p. 1206).

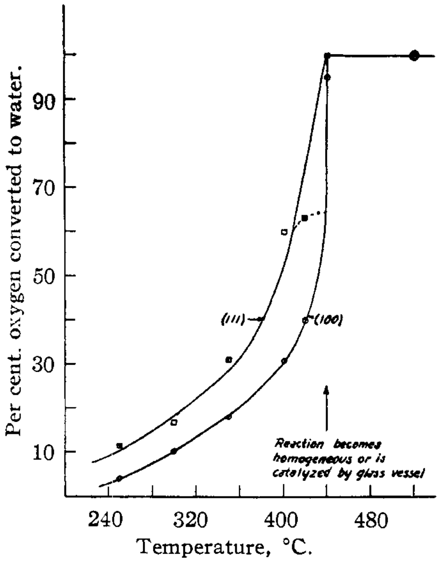
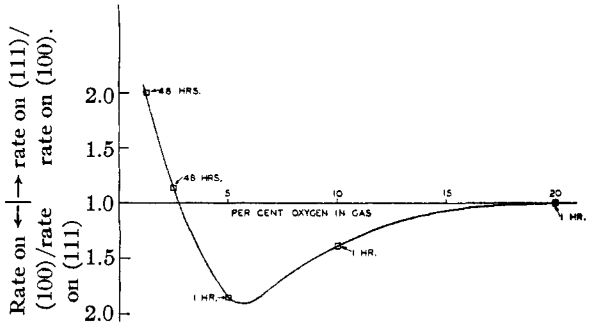


Fig. 13.—Curves showing change in rate of reaction with temperature: hydrogen–oxygen reaction on plane faces of a copper single crystal, total flow = 40 ml. per minute, O_2 concn. = 1.25%.

place appears as the dark elliptical-shaped region in the center of the face on the right since little light is reflected upward into the camera by the relatively smooth (111) surface. Microscopic views of the two faces are shown in Figs. 15 and 16.

Several experiments were carried out to determine the effect of the method of preparation of the starting surface on the rate of the reaction. It was found that within limits, as long as the base single crystal metal was exposed, the rates were independent of the exact surface preparation at the start. The reaction tended to form a surface characteristic of the face and reaction under consideration. For example, surfaces polished mechanically with alumina on felt, surfaces polished electrolytically, and surfaces roughened by etching electrolytically in a copper sulfate–sulfuric acid solution gave similar results after rearrangement. With an oxygen concentration of 1.25% and at a temperature of 400° the rate on the (111) face was twice that on the (100). In the case of the roughening of the surface by electrolytic etching, the area of the (111) face which had been exposed to the hydrogen and oxygen reaction for twenty-seven and one-half hours had become much smoother than the surrounding surface which had not been so exposed. The contrast between the two areas was very marked. In the case of the (100) face, since it is roughened by the catalytic reaction, the contrast between the two types of areas was not great, although a definite line of demarcation could be seen. When the (100) face was examined with a flashlight in a darkened room, brilliant reflections were visible from (110) facets in the reactive area but no reflections from (110) facets were obtained from the etched external area. Thus surfaces characteristic of the hydrogen and oxygen reaction were finally obtained regardless of the several different initial treatments given to the surface.

As the oxygen concentration was increased, the speed with which the rearrangement took place and the surface area exposed, especially on the (100) face, increased greatly. Figure 17 shows the ratio of the rates of reaction on the (111) and (100) faces with changes in oxygen concentration at 400°. As the oxygen concentration was increased below 5%, the rate on the (100) face relative to the (111) increased rapidly on account of the great increase in surface on the (100) face. No red powder formed within at least forty-eight hours. With oxygen concentrations of about 5% at which the powder began to form, the difference in rates between the two faces became increasingly less, until at 20% oxygen within one hour so much powder had formed on both faces that the inherent difference between the two faces was not detected. In order to obtain comparisons of the activity of the two faces as free as possible from powder, measurements were made at the higher oxygen concentrations after one hour of reaction. With an oxygen concentration of 20% the powder formed very rapidly at temperatures as low as 300°.



Hydrogen–oxygen reaction on plane faces of copper single crystal.

Fig. 17.—Ratio of rates of reaction on (100) and (111) faces with changes in oxygen concentration at 400°: total gas flow = 40 ml. per min.

Figure 18 shows the change in rates of reaction with time at 400° for two single crystal slices, for a single crystal slice which had been mechanically polished, and for an ordinary piece of polycrystalline copper which had been electrolytically polished. The increase in the rate of reaction on all samples corresponds to the visual observation of the formation of powder. As the reaction proceeded on the mechanically polished single crystal slice, the disturbed layer recrystallized to produce a polycrystalline surface which had a greatly increased rate.

A qualitative comparison of the degree of roughness on the (100) face at different oxygen concentrations was determined by the following procedure. The (100) face was exposed to definite mix

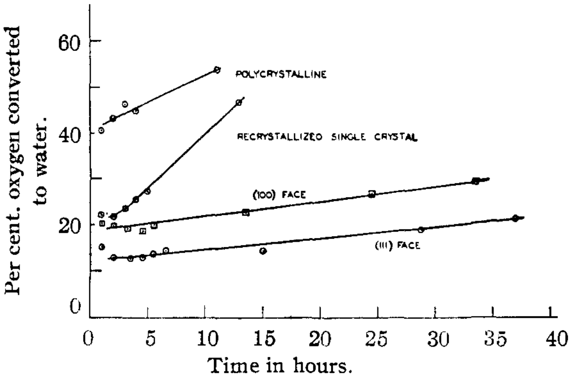


Fig. 18.—Change in rate of reaction with time at 400° and 10% oxygen concentration: gas flow = 40 ml. per min.

tures of hydrogen and oxygen for seven hours at 400°, and the surface was polished after each run with a suspension of levigated alumina on felt. The time necessary to polish away the roughened region was determined. Care was taken to insure equal conditions of polishing in each determination, and the results are shown in Table I.

Table I

% Oxygen in mixture	Time of polishing
1.25%	Less than 30 seconds
5.0	Approximately 50 seconds
10.0	Approximately 120 seconds
20.0	Greater than 240 seconds

In the case of the (111) face it took less than fifteen seconds to remove all traces of roughness under conditions at which no powder formed within seven hours.

Discussion

The discovery of a regular rearrangement of the catalyst surface under the influence of a gaseous reaction was made possible by the use of the catalyst in the form of a highly polished single crystal sphere exposing all possible crystal faces. The rearrangements showed themselves as highly complicated and symmetrical patterns which should be considered as records of the structure of the surface for a particular gas–metal reaction. On some faces definite facets parallel to one or more planes developed, on other faces a general roughening took place showing the development of no special planes, while other faces seemed to remain highly polished and apparently undisturbed. Although there were often similar features in the different patterns, in that the (100) face roughened greatly and the (111) remained relatively smooth, no two patterns for different gas–metal systems were found to be exactly the same.

In order to appreciate the significance of these regular surface rearrangements, it should be understood that they have been found with a number of reactions. The complications of these beautiful patterns and the differences between the patterns of different systems emphasize the complications of surface reactions and explain in part why they are so difficult to understand.

Not only does the pattern depend on the nature of the reactants, but for any one gas–metal system the pattern also depends on the conditions of experiment, such as temperature, concentration and rate of flow of the reacting gases, and time of reaction. As regards the latter, the planes developed in certain regions varied with time, emphasizing the importance of both rate and equilibrium factors in the rearrangement process. For example, with 14% oxygen at 400° (111) facets developed over a large region surrounding the (111) pole within twenty-four hours of reaction, but after a week of operation the size of the region containing the (111) facets had decreased considerably and the size of the region containing (110) facets had correspondingly increased. Also during the early period of the reaction a fine structure developed in many parts of the pattern, showing a variation in activity of many different faces, but after the reaction had proceeded for several days the complexity of the pattern was reduced and a fewer number of planes appeared. The crystal planes developed also depended on a certain critical angle between the plane in question and the surface of the metal specimen. In this connection it might be expected, if the rearrangement resulted simply from the heat evolved, that the most stable plane would be developed over the entire surface of the sphere, but facets parallel to a particular plane developed in one region, and, when the angle between the plane in question and the surface reached a certain value, facets parallel to another plane developed. In some regions several planes seemed to compete with each other for their existence.

It is surprising that these rearrangements, involving in some cases movement of the metal atoms over tremendous distances in terms of atomic dimensions, would take place so readily on massive metal at measured gas temperatures of only 400°, which is 680° below the melting point of the metal. The evaporation of considerable metal which deposited on the walls of the glass vessel suggested that the temperature of the metal surface was considerably higher than the measured gas temperature, but heating a crystal in hydrogen at 1000° failed to produce any rearrangement or evaporation. In fact a surface which has been roughened by this reaction may be "heat polished" by heating in hydrogen at such a high temperature. Therefore, high temperatures alone would not cause rearrangement or appreciable evaporation. Furthermore rearrangements have been obtained with an endothermic reaction. The evaporation of copper during the reduction of polycrystalline copper oxide has been attributed to the formation of steam between the grains and the expulsion of copper by the steam. In the copper single crystal surface used in these experiments there were no grain boundaries and no visible film of oxide. However, the (100) face which roughened greatly during the catalytic reaction is a face having a high rate of oxidation when heated in air.[6] The oxygen may possibly diffuse more rapidly down into the lattice of the (100) face and react to form steam which may then expel metal. Although the exact nature of such a catalyst surface was not known, these rearrangements indicated that the surface was in a state of great agitation, at least during the initial stages of rearrangement which lasted over a number of days for this particular reaction. These rearrangements which take place with catalytic reactions but not with adsorption indicate that the nature of the surface during such reactions may be quite different from that during adsorption. This fact in turn indicates that great care must be exercised in using adsorption measurements to interpret the nature of a catalytic surface of this kind.

One important experimental feature of these studies was that the reaction in effect prepared its own surface, and therefore reproducible surfaces exposing the structure of the base metal were obtained. In this method of study the use of light reflections, against a background of a single crystal sphere whose orientation was known, made it possible to identify the plane exposed right at the surface. The actual planes exposed at the surface cannot be determined by the diffraction of X-rays or electrons which penetrate the surface. The preparation of a catalyst surface with the aid of a gaseous reaction which produces a characteristic surface of a relatively well-known structure offers the possibility of standard surfaces for experimental studies.

One interesting effect of these rearrangements is that a surface originally prepared parallel to an unreactive plane may finally become a very active surface per unit starting area since both a greater total area and/or different facets may be finally produced. This suggests the possibility of preparing a surface parallel to one plane and then activating it by reaction with one set of gases for use with another set. In order to obtain appreciable adsorption on platinum Langmuir[7] found that it was necessary to activate the surface by means of the reaction of hydrogen and oxygen. Obviously this treatment increased the surface area, but it was not known whether special facets developed.

The alteration of the pattern on copper by the addition on the surface of small amounts of a second metal, such as zinc or nickel, indicates that the action of a promoter in some cases is to control the planes developed.

During the study of rates several different slices as well as the spherical specimen containing both faces were used. Similar results were obtained on all samples of the same face.

Since the structure of the surface continued to rearrange over a considerable length of time depending on the conditions of the experiment, the rate measurements must be considered in relation to these structural changes. There is no simple method of measuring the true surface area of small specimens, and it was elected to report the rate measurements, unless otherwise stated, in terms of the apparent starting area which in all cases was 2.69 sq. cm. This method of reporting rates enabled the more important facts to be arrived at and the minimum values for the relative rates on the two faces to be given. It is planned to measure surface areas, but this in itself is a major undertaking for these small specimens.

At low concentrations of oxygen in the neighborhood of 1%, where the rearrangements were relatively slight, the rate on the (111) face was approximately twice that on the (100) face. Since it can be seen in Figs. 14–16 that the surface on the (100) face was much rougher, and therefore had a much greater final surface than the (111), the actual rate on the (111) face per unit of final surface must have been considerably greater than twice the rate on the (100) face per same unit. It would appear that the surface on the (100) face was at least twice that on the (111) face at this concentration, and this estimate would make the rate on the (111) face per unit of final surface at least four times that on the (100). The rates on only two different faces were measured in these studies, and there may be others which have greater or lower rates.

As the concentration of oxygen was increased and the (100) face became much rougher than the (111), it would be expected that the rate on the (100) would become greater than that on the (111), although the rate per unit of final surface might still be greater on the (111) face. As the oxygen concentration was increased still higher and powder began to form, the surface of the powder was so much greater than that of the base metal that most of the reaction took place on the powder and the rates on the two faces became approximately equal as would be expected. The underlying pattern could still be seen when most of the powder was removed.

Summary

The catalytic reaction of hydrogen and oxygen on a single crystal of copper has been studied. Single crystals in the form of spheres exposing all possible faces and in the form of slices parallel to a particular face were used. The crystals were mechanically and electrolytically polished and annealed in hydrogen so that the surface of the base crystal was exposed to the action of the gases. With oxygen concentrations of 1–20% at 400° regular rearrangements were found to take place in the surface of the metal, exposing certain facets on some faces, roughening others without the development of particular planes, while other faces remained quite smooth and were apparently undisturbed. Rate measurements were made on

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[6] Gwathmey and Benton, *J. Phys. Chem.*, **46**, 969 (1942).

[7] Langmuir, THIS JOURNAL, **40**, 1361 (1918).

(100) and (111) faces, and it was found that appreciable differences in rates existed between the two faces. These differences depended on both the differences in activity per unit of surface and on the differences in total surface area exposed on the two faces. The rate measurements were correlated with the structure of the surfaces as the surfaces rearranged under the action of the catalytic reaction.

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The Selective Deposition of Carbon on the (111) Face of a Nickel Crystal in the Catalytic Decomposition of Carbon Monoxide[1]

BY HENRY LEIDHEISER, JR., AND ALLAN T. GWATHMEY

Previously reported results[2] have shown that the catalytic reaction of hydrogen and oxygen leads to rearrangement of a copper surface and proceeds at a rate dependent on the crystal face exposed to the reacting gases. Results reported herein give an example of a catalytic process which does not lead to visible rearrangement of the surface initially and which proceeds at a rate dependent on crystal face.

A monocrystalline sphere[3] of nickel, 0.5 in. in diameter, with a shaft, $^3/_{16}$ in. in diameter and $^3/_8$ in. long, on one side was mechanically polished and then electrolytically polished by the method of Hothersall and Hammond[4] in order to give a smooth and strain-free surface. It was heated to 550° in carbon monoxide at a pressure of one atmosphere in an electric furnace provided with a window for continuous observation. After ten hours the pattern shown in Fig. 1 (see insert facing page 1203) began to develop. Black deposits had formed in large areas around the (111) poles but not in areas at the (100) and (110) poles. As the reaction continued the diameter of the (111) areas increased until the deposit covered the entire surface with the exception of a small square at each (100) pole and a narrow band between neighboring (100) poles and running through (110) poles. The photograph shows in a striking manner that the decomposition of carbon monoxide to form carbon on nickel at 550° proceeds at widely different rates on the (100) and (111) faces. The black deposit was readily removable by rubbing with tissue within several hours after it was first observed. As the reaction continued, however, the deposit tenaciously adhered to the surface, and it could not be removed by rubbing.

Evidence summarized by Hofer[5] indicates that when nickel is treated with carbon monoxide above 500° the major product left on the surface is carbon, although the presence of an intermediate carbide is not excluded. In order to obtain a sufficient amount of deposit for analysis, a polycrystalline nickel foil of larger surface area was treated with carbon monoxide under identical conditions as the single crystal. The analysis of the product on the surface was as follows: carbon 88.52 wt. %, nickel 11.01 wt. %. This analysis corresponds to approximately 97.5 atom % carbon and 2.5 atom % nickel.

Results similar to those shown in Fig. 1 were obtained at 550° in mixtures of hydrogen and carbon monoxide when the carbon monoxide was in excess. When the carbon monoxide was present in low concentrations in the neighborhood of 10%, no carbon deposit was observed and rearrangement patterns resulted.

It is interesting that the crystal lattice of graphite may be superimposed on the (111) face of nickel with only slight distortion. No similar match is possible on the (100) or (110) faces of nickel. It should be pointed out, however, that even though the (111) face of copper would give almost as good a match, no carbon deposits were visible after forty-eight hours at 550°.

Information on the deposition of carbon is important in an understanding of the Fischer–Tropsch catalytic process, and the results herein reported indicate the importance of crystal face in reactions of this type.

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[1] This work was supported by a grant from the Research Corporation.

[2] Leidheiser and Gwathmey, THIS JOURNAL, **70**, 1200 (1948).

[3] See Gwathmey and Benton, *J. Phys. Chem.*, **44**, 35 (1940), for a description of the technique for growing and machining single crystals.

[4] Hothersall and Hammond, *J. Electrodepositors' Tech. Soc.*, **16**, 83 (1940).

[5] Hofer, U. S. Bur. Mines Rept. Investigations 3770, 39 pp. (1944).