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

The Formation of Powder and its Dependence on Crystal Face during the Catalytic Reaction of Hydrogen and Oxygen on a Single Crystal of Copper[1]

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When a four to one volume ratio of hydrogen to oxygen at a gas flow of 17 cc. per minute reacted catalytically at 400°, a red powder formed on the surface in time. The rate of powder formation depended on the crystal face exposed at the surface, being greatest on the (100) face, least on the (111) face and relatively low on the (110) face. Powder became visible on the (100) face at the end of four hours of reaction, while no powder had formed on the (111) face at the end of thirty days.

Introduction

When a single crystal of copper in the form of a sphere was used as a catalyst for the reaction of hydrogen and oxygen to form water in the temperature range of 300 to 400°, the surface underwent a regular and reproducible rearrangement in which facets of definite crystallographic orientation were developed.[3] With oxygen concentrations greater than approximately 5% the surface in time also became covered with a loosely adherent powder. The greater the oxygen concentration the more rapidly the powder formed. The object of the present investigation was to determine whether the rate of formation of powder depended on crystal face.

Method of Experiment.—A single crystal sphere of copper, $^{5}/_{8}$ inch in diameter and with a shaft $^{1}/_{4}$ inch in diameter and $^{1}/_{2}$ inch long, was prepared by a method previously described.[3,4] The crystal was polished electrolytically,[3] washed in running tap water for four minutes, dried with tissue and placed in the reactor. The reactor consisted of a glass bulb which was located in a furnace having a small window for observing the crystal, and purified gases were passed over the crystal held by a glass tube in the center of the bulb. The crystal was heated in hydrogen for at least two hours at 550° prior to the experiment in order to reduce any oxide. The temperature was then lowered to 400°, and oxygen was admitted to the stream of hydrogen in the ratio of one volume of oxygen to four volumes of hydrogen.

Results.—Soon after the hydrogen–oxygen mixture was admitted, the surface of the crystal was roughened in certain regions as previously described.[3] Within three to four minutes a sharply outlined pattern could be observed. This pattern was due to the development of definite facets in the large region around the (111) face as revealed by reflections when a beam of light was directed normal to the surface at the (111) face. As the reaction proceeded, the development of facets became more pronounced in the large region around the (111) face while the small region immediately at the (111) face remained smooth. The (100) region formed facets of several orientations. At the end of about 16 hours, the principal facets which formed in the (100) region were parallel to the (111) and (110) planes as revealed by light reflections. The term, region, is used to refer not only to the surface immediately at a particular pole but also to the regions adjacent to this pole. The sizes of these regions will depend on the conditions of experiment and are generally shown on the photographs.

When the reaction was allowed to proceed for three to four hours at a total rate of gas flow of 17 cc. per minute, a reddish powder formed on the (100) region, while the small (110) and (111) regions remained bright and shiny giving good reflections when a light was directed normal to the surface at these faces. The powder on the (100) region could be easily removed from the surface by brushing with a camel's-hair brush. When the reaction proceeded for 10 to 12 days, powder formed over the entire surface of the crystal with the exception of small (110) and (111) regions. Figure 1 shows a view normal to a (111) face of a crystal which has undergone the hydrogen–oxygen reaction for 12 days. Four (111) regions may be seen. One of these is located at the center of the picture and the other three are shown as regions at the outer periphery which are 120° from each other. Three (110) regions are also shown in Fig. 1. These are the long, narrow, dark regions located approximately half-way between the center (111) region and the three (111) regions on the outer periphery of the sphere.

A prolonged reaction for 30 days produced powder over the entire surface of the crystal with the exception of the small (111) regions. A photograph of a crystal after undergoing reaction for 30 days is shown in Fig. 2. Figures 3 and 4 show photomicrographs of the final surface structures.

The red powder was removed from the crystal surfaces, and X-ray diffraction photographs were taken. The diffraction pattern showed the composition of the powder to be largely copper. A small amount of cuprous oxide was present, but it is thought that this formed during the cooling in the gas mixture. Under the conditions stated, there was no visible oxide on the surface at any time during the reaction. An electron micrograph of the powder[5] is shown in Fig. 5.

Discussion

The type of facet and the amount of powder formed on any one face were a function of time, temperature, oxygen concentration and gas flow. It is interesting that neither facets nor powder formed on the close packed (111) face during the reaction. However, powder formed rapidly on the (100) face and area immediately around the (100) face. These were the regions which roughened initially because of the development of facets of several orientations. Polycrystals tend to form preferentially on the (100) face in several other reactions of copper. In electroplating copper from a copper sulfate solution on to a single crystal of copper at low current density, polycrystals formed on the (100) face while the deposit on other faces tended to be monocrystalline.[6] And when a single crystal of copper was heated to a red heat and suddenly quenched in water, polycrystals formed only at the (100) face.

During the initial facet formation, in the hydrogen–oxygen reaction, small pyramids seemed to form on the (100) region. These projections showed specular reflections in certain definite directions and at the end of about 16 hours, the principal reflections were from facets parallel to the (111) and (110) planes. As the reaction proceeded, the reflections from the (100) region diminished and finally disappeared altogether because of powder formation. However, if the powder was removed,

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[1] This work was supported in part by the Office of Naval Research under Contract No. Nonr-474/01, NR 036-010.

[2] Holder of The Texas Company Fellowship, 1951–1953.

[3] H. Leidheiser and A. T. Gwathmey, THIS JOURNAL, **70**, 1200 (1948).

[4] A. T. Gwathmey and A. F. Benton, *J. Phys. Chem.*, **44**, 35 (1940).

[5] Electron micrographs were made by the Virginia Institute for Scientific Research, Richmond, Virginia.

[6] H. Leidheiser and A. T. Gwathmey, *Trans. Electrochem. Soc.*, **19**, 97 (1947).

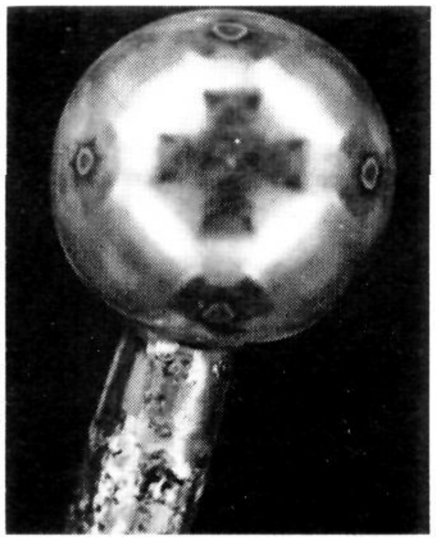
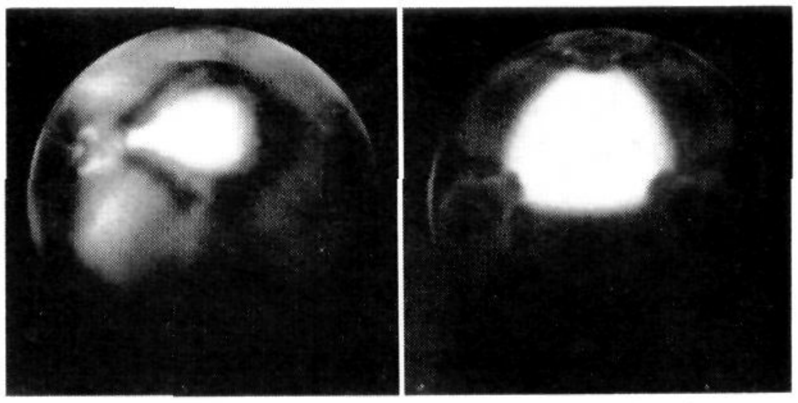
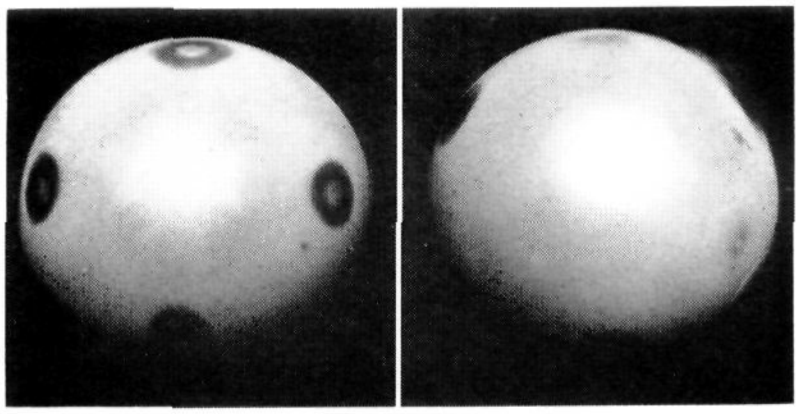


Fig. 1.—Rearrangement pattern of a copper single crystal with no added solid. Photograph taken with four lights to show symmetry and detail of the pattern. Note that the end of the shaft is polycrystalline.



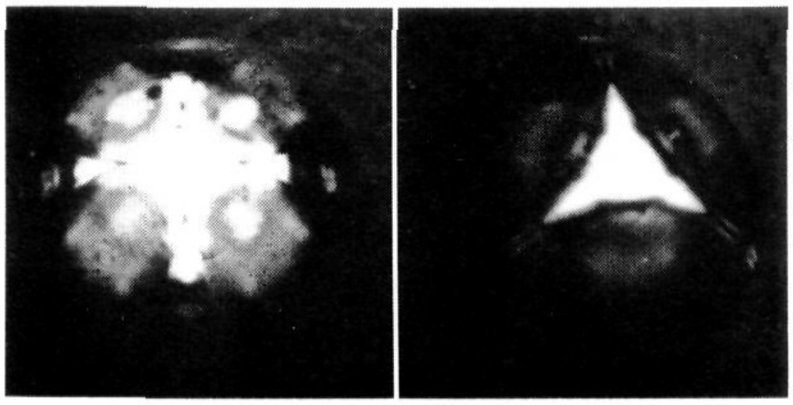
2A. Normal to (100) face. 2B. Normal to (111) face.

Fig. 2.—Rearrangement pattern with no solid added to the surface. Crystals in Figs. 2, 3, 4 and 5 were illuminated with one light.



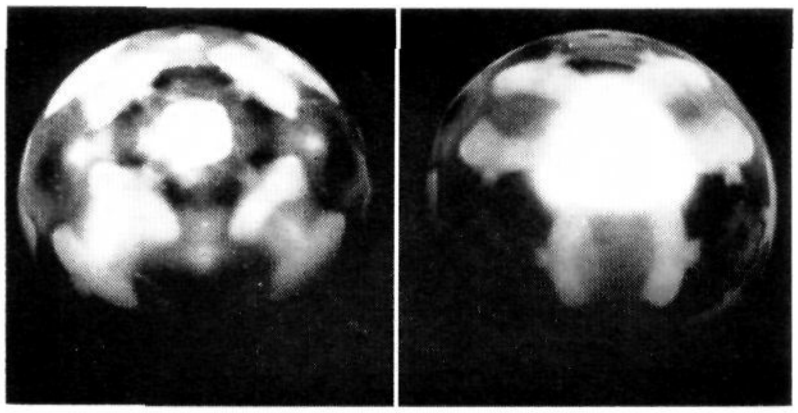
4A. Normal to (100) face. 4B. Normal to (111) face.

Fig. 4.—Rearrangement pattern when zinc is electrodeposited on the surface.



3A. Normal to (100) face. 3B. Normal to (111) face.

Fig. 3.—Rearrangement pattern when silver is added to the surface.



5A. Normal to (100) face. 5B. Normal to (111) face.

Fig. 5.—Rearrangement pattern with chromium trioxide added to the surface.

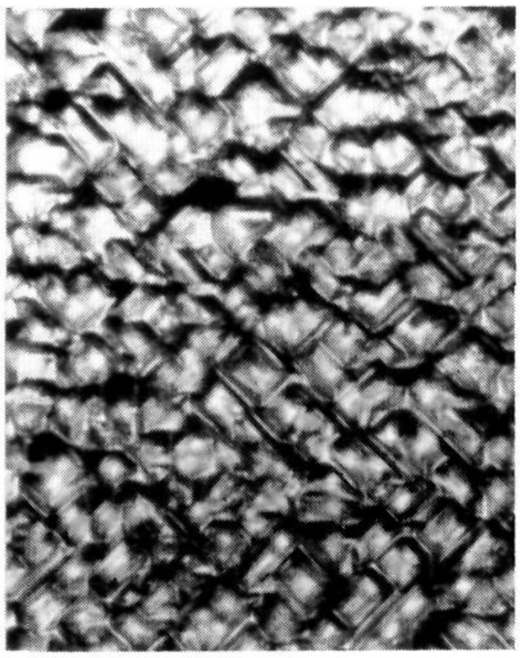


Fig. 6.—Effect on a (100) face of copper of a 19:1 mixture of hydrogen and oxygen at 400° for 18 hr. The sides of the pyramids are (110) facets; 1050×.

Fig. 1.—Normal to (111) face. Note absence of powder on (111) and (110) regions after 12-day reaction.

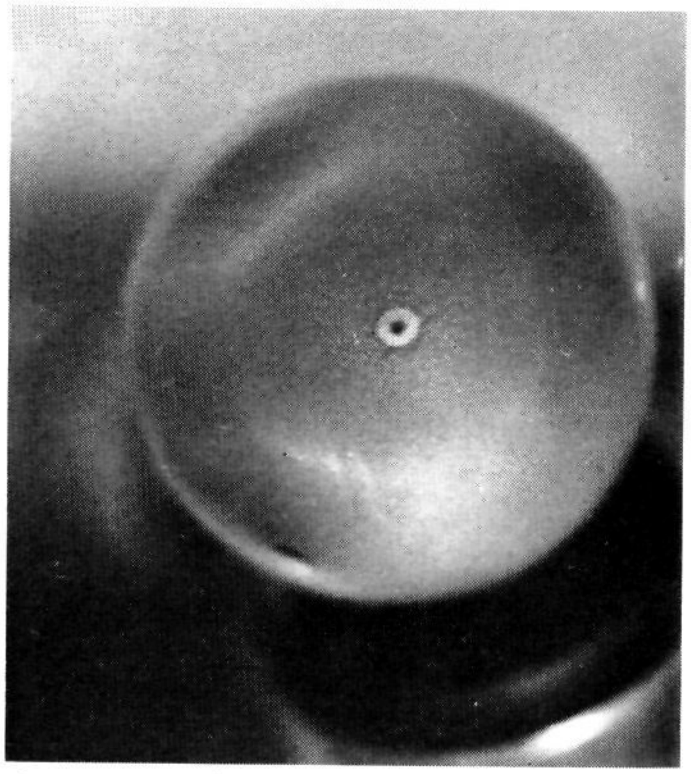


Fig. 2.—Normal to (111) face. Note absence of powder on (111) region after 30-day reaction.

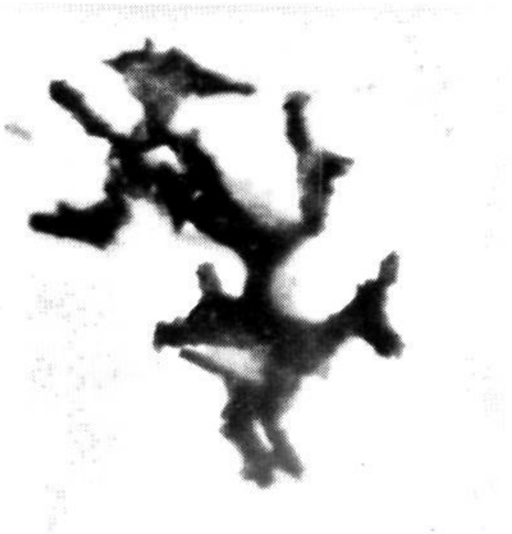


Fig. 5.—Photograph of a particle of powder removed from the (110) region, magnification 20,000×.

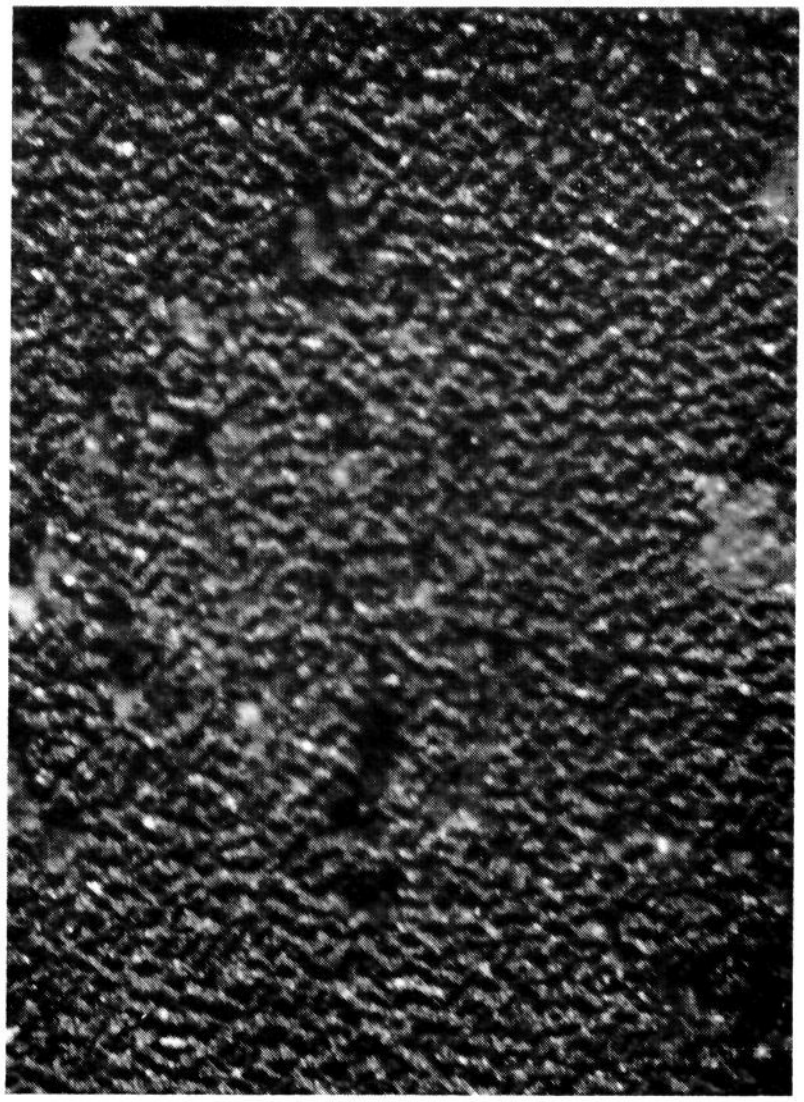


Fig. 3.—Photomicrograph of (100) region after 30-day reaction, 155×.

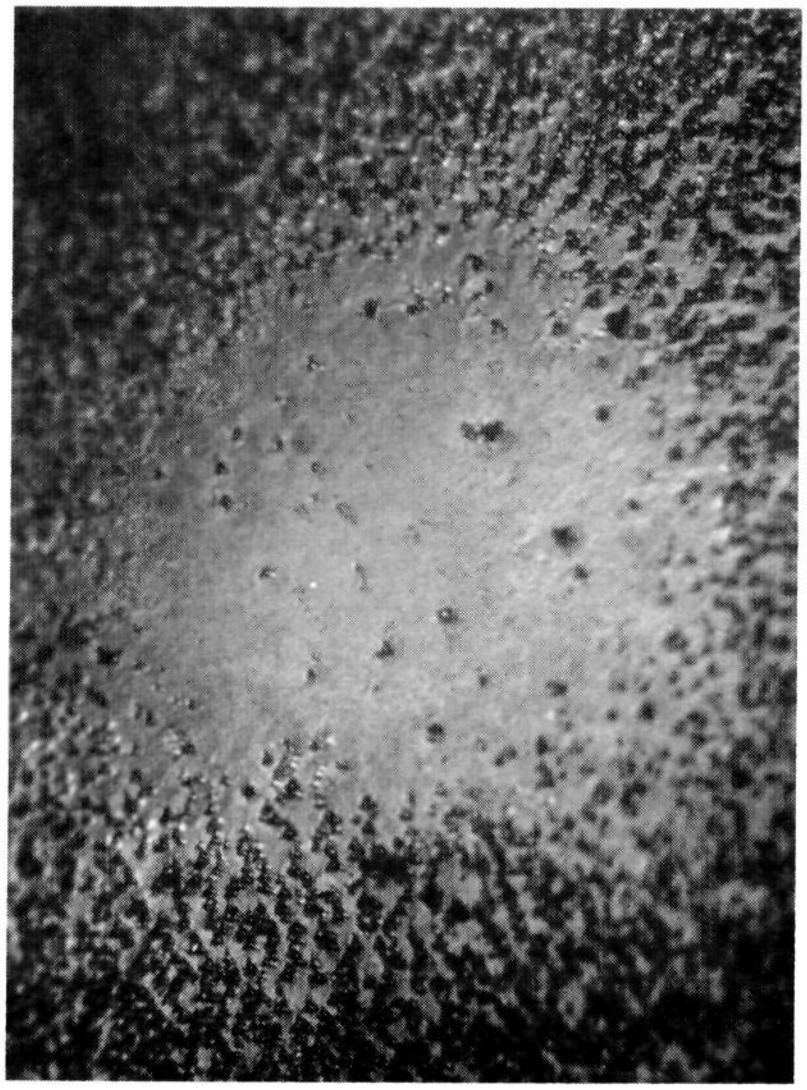


Fig. 4.—Photomicrograph of (111) region after 30-day reaction, 155×.

the surface underneath possessed a regular, rearranged structure which gave bright reflections in certain directions with a light directed at the surface.

This formation of powder from a massive single crystal during a catalytic reaction is an interesting case of crystal growth, since the reverse process of growth from powder to larger particles would ordinarily take place under the influence of heat. The question of whether there is any fundamental relation between contact catalysis and powder formation should be considered in future studies.

In hopes of understanding the manner of powder formation, the various surfaces were studied with the optical microscope after different reaction times. The powder appeared to form first as small projections at the outer edge of the steps or facets which developed in certain specific crystallographic regions. Further studies of the manner of formation of the powder are being made with the aid of an electron microscope.

There are examples of powder formation from massive polycrystalline catalysts such as from platinum used in the catalytic oxidation of ammonia.[7] Rideal and Taylor also state that a photomicroscopic study of platinum gauze used as a catalyst for the oxidation of ammonia "indicates that there is a gradual increase in catalytic activity associated with the formation of minute craters on the metal, the lip of each crater being just tinged with "grey" or "black" platinum."[7] Turkevich carried out an electron-microscope study of polycrystalline catalyst surfaces and reported the formation of cubes, one micron on an edge, on platinized asbestos used for the hydrogen–oxygen reaction.[8]

During the course of the hydrogen–oxygen reaction considerable evaporation of copper occurred, and the copper was deposited on the glass in the reactor several centimeters from the copper single crystal. It would be expected that the surface atoms would be held more loosely than atoms in the interior and that under the influence of the large energy of this reaction, diffusion and evaporation would occur.

In addition to the hydrogen–oxygen reaction on copper, there are several other catalytic reactions in which metal atoms are moved considerable distances from their original lattice positions. For example, in the case of the formation of carbon on the (111) face of a nickel single crystal heated in carbon monoxide, an appreciable amount of nickel was found in the carbon.[9] In the reaction of acetylene on copper oxide to form cuprene, appreciable amounts of copper were found in the cuprene at great distances in terms of atomic dimensions from the copper oxide surface.[10]

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[7] E. K. Rideal and H. S. Taylor, "Catalysis in Theory and Practice," 2nd ed., The Macmillan Co., New York, N. Y., p. 176.

[8] J. Turkevich, *J. Chem. Phys.*, **13**, 235 (1945).

[9] H. Leidheiser and A. T. Gwathmey, THIS JOURNAL, **70**, 1206 (1948).

[10] J. H. L. Watson and K. Kaufmann, *J. Appl. Phys.*, **17**, 996 (1946).

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

The Influence of Foreign Atoms on the Surface Rearrangement Produced by the Catalytic Reaction of Hydrogen and Oxygen on a Single Crystal of Copper[1]

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The effect of foreign atoms on the surface rearrangement produced by the catalytic reaction of hydrogen and oxygen on single crystals of copper has been described. These added substances may control the regrowth of the surface by changing the orientation of the facets developed or by causing formation of copper powder on the surface. Rearrangement of the surface cannot be the result of temperature alone, but must result from the strain and energy applied to the surface by adsorption and reaction, and is controlled by the geometry and electronic properties of the surface and the gases present. Since catalytic reaction rates on a metal vary with crystallographic face, it is indicated that one means of promoter action is to control the orientation of the facets exposed by the catalyst surface.

Introduction

When a single crystal of copper in the form of a sphere was used as a catalyst for the reaction of hydrogen and oxygen to form water, the surface underwent a regular and reproducible rearrangement in which facets of definite crystallographic orientation were developed.[2] Under certain conditions and after longer periods of time, the surface became covered with loosely held copper powder.[3] Some evidence[2] was obtained which indicated that the addition of a small amount of a second metal to the surface altered the rearrangement. The purpose of this paper is to describe experiments which conclusively show that very small amounts of certain metals or metallic oxides on the surface of a copper single crystal will control the type of rearrangement which takes place during a catalytic reaction.

Experimental Procedure

Single crystal copper spheres,[4] $^5/_8$ in. in diameter and with a shaft $^1/_4$ in. in diameter and $^1/_2$ in. long for handling, were prepared and polished by the method previously described.[5,2] The foreign solid was then added to the surface either by dipping the sphere in an appropriate solution (to allow adsorption, chemical reaction, or wetting of the sphere by a

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[1] This work was supported by the Office of Naval Research under Contract No. Nonr-474/01, NR 036-010.

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

[3] *Cf.* paper on powder formation by J. B. Wagner, Jr., and A. T. Gwathmey, *ibid.*, **76**, 390 (1954).

[4] The machined spheres were obtained from the Virginia Institute for Scientific Research, Richmond, Virginia.

[5] A. T. Gwathmey and A. F. Benton, *J. Phys. Chem.*, **44**, 35 (1940).