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]

[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).

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[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]

BY ROBERT E. CUNNINGHAM AND ALLAN T. GWATHMEY

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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.[5,6] 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

[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).

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[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).

film of the solution), or by electrodeposition, or by evaporating metals onto the surface. The latter two methods were preferred since known amounts of material could be added to the surface. The crystal was then heated in hydrogen at 500° for at least one hour to reduce any oxide and to help relieve any residual strain from the mechanical polishing. The system was cooled to 350° and oxygen admitted to the gas stream. The total gas flow was about 40 cc. min.$^{-1}$, of which 12.5% was oxygen and the balance hydrogen. The catalytic formation of water on the metal crystal was continued for a period of 16 to 18 hr. and the crystal cooled in an atmosphere of hydrogen. Photographs were taken generally using a single beam of light reflected from one of the principal faces, so that the development of facets parallel to this face could be seen. This standardized illumination of the crystal was also necessary so that the different patterns could be directly compared.

Results

Figures 1 and 2 show the rearrangement pattern obtained on a pure copper single crystal sphere when no foreign atoms were added to the surface. In Fig. 1 the crystal was illuminated with four lights in order to show the full detail and symmetry of the pattern, while in Fig. 2 the crystal was illuminated with a single light so that the pattern as seen could be compared with those shown in Figs. 3, 4 and 5.

Figure 3 shows the effect of silver added to the surface. The silver was added by metal replacement from very dilute (*ca.* 10^{-5} *m*) solutions of silver nitrate. Essentially the same pattern was obtained by the evaporation of a 5 Å. layer of silver onto the crystal from platinum wire. The pattern obtained was quite definite, even though the facets developed differed from those obtained when no foreign atoms were added to the surface. This pattern was intricate in its fine detail which cannot be shown in a few photographs.

Figure 4 shows the effect on rearrangement of a layer of zinc (of average thickness 20 Å.) electrodeposited on the crystal surface from a 1 *m* zinc nitrate solution. Copper powder formed over the entire surface except in the neighborhood of the (111) poles. The powder was less dense in the areas around the (100) poles. Since the powder formed was not oriented crystallographically with respect to the original metal, the specificity of the pattern was lost in the areas covered. However, the powder could easily be wiped off with a soft tissue, revealing a rearranged surface which was different from that of pure copper.

Figure 5 shows the effect of chromium trioxide added to the surface by dipping the crystal into a 1 *m* chromium trioxide solution and then wiping the surface with a soft tissue. The pattern remained fairly specific except in certain areas (the four dumb-bell shaped areas in Fig. 5A) which became covered with powder. The remaining surface, as in the case of rearrangement with silver on the surface, displayed a very complex pattern.

Discussion

In general the photographs show that small amounts of a metal or metallic oxide added to the surface of a copper single crystal modified the rearrangement of the surface either by controlling the development of certain facets, or by promoting the formation of copper powder at different rates on the different faces. The term "rearrangement" is used in this paper to describe the change in the surface which results in visible roughening, generally with formation of facets parallel to certain crystal planes.

The microscopic appearance of a rearranged (100) face is shown in Fig. 6. The final surface of the rearranged crystal was independent of the smoothness of the initial surface within certain limits, and to this extent the catalytic reaction prepared its own surface. The rearrangements were regular, and except in the case of powder formation, X-ray diffraction studies indicated that the rearranged surface was crystallographically continuous with the base metal.

Temperature alone is not sufficient to produce these rearrangements. In fact, heating in hydrogen at 500 and at 1000° [2] resulted in "polishing" of rearranged surfaces. Rearrangement of a catalytic surface must be considered a special case of crystal growth which utilizes the energy released by the reaction and which is controlled by the geometry and electronic properties of the surface, reactants and products. The rearrangement patterns obtained were specific for the metal and gases used and for the conditions of experiment employed. Thus the surfaces which developed during the reaction were generally not those which would develop on a crystal in equilibrium with its vapor.

In regard to the movement of the metal atoms over the surface, it seems reasonable that the strain applied to the metal by adsorption of the gases and the energy supplied by the reaction could produce a state in which a large number of metal atoms were disturbed and only loosely held by the surface. Metal atoms which have become isolated on top of an atomically dense plane by this strain and energy can share only a few bonds with the surface and must diffuse to a more favorable position, evaporate, or agglomerate to regain stability. Since evaporation and diffusion can be abnormally rapid on a surface acting as a catalyst, the rearrangement phenomenon is not too surprising even though it involves the movement of metal atoms over large distances relative to atomic dimensions. In these catalytic experiments evaporated copper was always found on the walls of the glass vessel.

It is probable that foreign atoms on the surface act in more than one way to control the rearrangement. They may change the electronic properties of the various faces, or enter into one step of the reaction, or interfere physically with regular crystal growth. In the case of silver added to the surface, since silver oxide is easily reduced and silver is completely soluble in copper, it seems probable that the small amount added was dissolved in the surface layer of the copper. The silver atoms may have acted to control the rearrangement by changing the electronic properties of the crystal faces. Alternately the silver atoms may have tended to accumulate on certain crystal faces, thus controlling their growth. Experiments made in this Laboratory with radioactive silver indicated no long range movement (of the order of mm.) of silver to particular areas on the single crystal surface, but the accumulation on facets of certain orientation would not have been detected by the method used.

In the case of zinc and chromium trioxide, it is to be expected that oxides of these elements (or copper chromite) were present during the reaction. These materials may have interfered with regular crystal growth, since they would not fit into the copper lattice, and thus induced the formation of powder.

The control of the rearrangement pattern by foreign atoms on the surface suggests that one role of a promotor is to control the orientation of the facets produced on the catalytic surface. Many chemical reactions, including catalysis, have been shown to vary markedly with crystal face,[6,2] and materials which alter the crystal faces exposed should change the catalytic properties of the metal even if the added material itself has no effect on the reaction.

It should be pointed out that, with exception of evaporated silver, the foreign metal and metallic oxides which were added in these experiments were not evenly distributed over the surface of the crystal. The patterns obtained, therefore, reflect in part this distribution. The experiments with silver added both uniformly and non-uniformly indicate, however, that the change in pattern is not due just to the distribution of the added material on the surface. Because of the dependence of rate of surface processes on crystal face, difficulty will always be encountered in crystal growth processes in getting an evenly distributed layer of foreign atoms on all faces.

Measurements are now being made of the rates of reaction of hydrogen and oxygen on different faces of a copper single crystal to which foreign metal atoms have been added. These results, together with a more detailed description of the rearranged surfaces, will be presented in a later paper.

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(6) See A. T. Gwathmey, H. Leidheiser, Jr., and G. P. Smith, NACA Tech. Note No. 1460, June, 1948, for a discussion of the influence of crystal face on chemical activities of single crystals of metals.

[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES (A DIVISION OF SOCONY-VACUUM OIL CO., INC.) RESEARCH AND DEVELOPMENT DEPARTMENT]

Ternary Systems with Two Separate Binodal Curves[1]

BY ALFRED W. FRANCIS

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Several ternary systems with two separate binodal curves have been found. The components are an aliphatic solvent, an aromatic solvent, and a non-aromatic hydrocarbon with critical solution temperatures not very different with the two solvents. One system, methanol–nitrobenzene–2,2,4-trimethylpentane, has been studied at several temperatures. The two curves meet at both plait points at 14.1°, the "col" temperature. The isotherm at this temperature resembles lines intersecting at a finite angle, not curves with a common tangent.

Only one ternary system with two separate binodal curves, that of water–ethanol–succinonitrile,[2] is described in the chemical literature. In that system two of the components freeze before the curves merge. The manner of coalescence of two separate binodal curves has not been observed previously.

Conditions for existence of these systems are indicated in a solid diagram of a ternary system of A, B and C in the shape of a triangular prism with the vertical axis denoting temperature. Suppose A and B are miscible at all temperatures considered, but C has a limited miscibility with either A or B up to the respective binary critical solution temperatures. These are the tops of the parabolic curves showing binary miscibilities against temperature for systems of C with A and B (Fig. 1). The binodal surface in the solid diagram is a ridge across the prism connecting these two curves. If A and B are similar chemicals, *e.g.*, both aromatic solvents, the ridge is practically straight, though in general sloping. If A and B are dissimilar, the ridge is usually concave upward; and if the two critical solution temperatures are fairly close together, within 20 to 40°, there may be a saddle point which is lower than either end. By analogy with a mountain pass it will be convenient to call this point a "col" (low point of the ridge). Under these conditions and in the temperature range between this col and the lower of the two critical solution temperatures, the isothermal diagram shows two separate binodal curves.

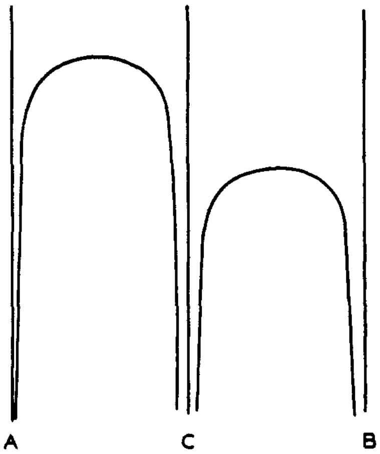

Fig. 1.

Examples are listed in Table I. "C.S.T." are critical solution temperatures between the two substances in adjacent columns. Several other

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(1) Presented before the Division of Physical and Inorganic Chemistry at the 124th Meeting of the American Chemical Society, Chicago, Ill., September 7, 1953.

(2) F. A. H. Schreinemakers, *Z. physik. Chem.*, **27**, 95 (1898). A related system water–phenol–salicylic acid with one curve almost submerged by a solid phase equilibrium was reported by C. R. Bailey, *J. Chem. Soc.*, 1951 (1925).