

Surface Heterogeneity of Metals of the Copper Group in the Catalytic Decomposition of Hydrogen Peroxide

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Received December 16, 1968

A certain heterogeneity of the surface of metals of the copper group has been observed in the decomposition of hydrogen peroxide. The distribution curves of the active centers with respect to their activation energy have been obtained. It has been established that there are active centers having different activation energy on the surface of both single crystals and polycrystalline samples. The faces (100), which are more closely packed, are characterized by lower activation energy. Thermal treatment of silver in air or under vacuum produces changes in the values of the most probable activation energy of the process. This phenomenon is connected with the amount of oxygen on the surface and in the bulk of silver.

INTRODUCTION

There are many experimental data in the literature showing that the crystallographic faces of a crystal differ in their catalytic activity (1-8). This could be one of the principal causes for the biographical heterogeneity of the surface of various polycrystalline and porous catalysts and adsorbents. For that reason average results are usually obtained for the activity of such samples and the spectrum of the active sites remains unknown. There arises now the question to what extent the separate faces of a single crystal are homogeneous with regard to their catalytic properties and what is the possible spectrum of their activity.

In previous work (9), a method for studying microsites of the catalyst surface by decomposition of hydrogen peroxide was proposed. In the present investigation, the same method is applied for studying the heterogeneity of the catalytic properties of some metal polycrystalline surfaces. Our purpose is to show the heterogeneity of the surfaces as well as to obtain the distribution curves of the active centers with respect to the corresponding activation energy. We investigate further two types of faces of a silver single crystal and obtain the corresponding distribution curves.

EXPERIMENTAL

A metal plate previously treated (polished, cleaned, and heated) was placed in a small glass vessel (kept at constant temperature) situated in the visual field of a microscope of little magnification. A diluted solution of hydrogen peroxide (0.02 *M*) was added at comparatively low temperature (283°K) and the time of the beginning of the reaction was marked. The diameters of some bubbles formed on the surface of the plate were measured in equal periods of time (Fig. 1) using an ocular micrometer or after photographing the bubbles. The temperature of the solution was smoothly raised and its values were determined with an accuracy of $\pm 0.1^\circ\text{C}$ simultaneously with the measurements of the bubble diameters. In about 20 min the temperature was raised by 25-30°C and the diameters of the bubbles increased considerably. By the end of the experiment only a negligible part of the peroxide was decomposed so that the reaction was practically of zero order. The rate of the process was judged by the volume (reduced to normal conditions) of the oxygen evolved in a bubble for a unit of time.

The relationship d^3/T versus t is a gradually increasing function (Fig. 2). The



Fig. 1. Oxygen bubbles on polycrystalline silver surface.

rate constant of the process for a given temperature may be determined by graphical differentiation. In all studied cases the experimental data follow strictly the Arrhenius' relationship (Fig. 3). By this method, the activation energy is quickly determined for each bubble. For a given site

of the surface, the activation energy values vary by no more than 5%.

The activity of single-crystal faces was studied on a sample obtained by electrocrystallization in the same way as in the work of R. Kaischew and co-workers (10, 11). The single crystal, well washed, was previously treated in air at 623°K for 2 hr.

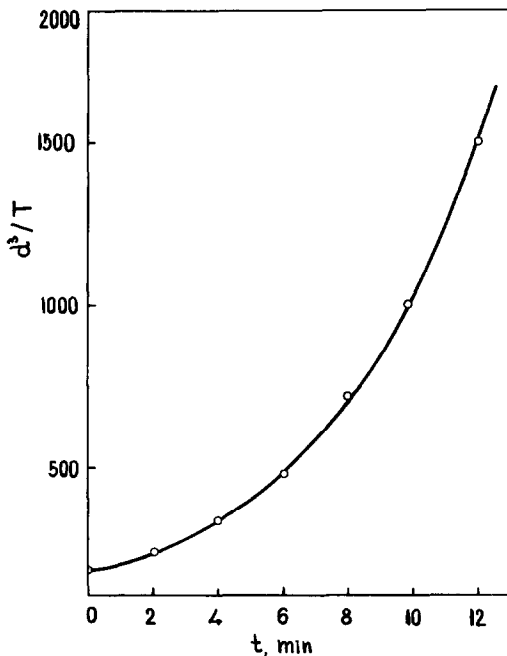


Fig. 2. Increase of the diameter of an oxygen bulb with the time.

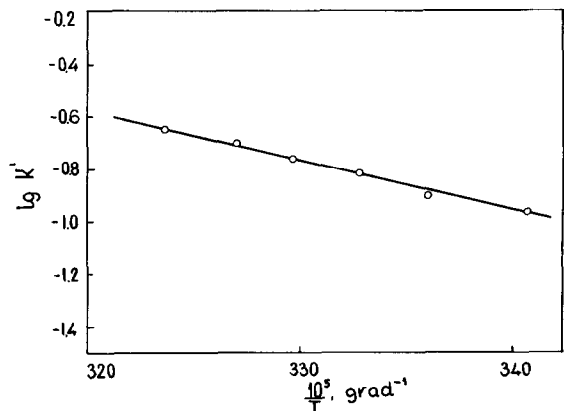


Fig. 3. Arrhenius' relationship.

RESULTS AND DISCUSSION

The investigations of Bliznakov and Peshev (12, 13) established that silver plates exhibit different activities after heating them in air in the temperature range of 473° to 1123°K. The values obtained for the activation energy of the process vary

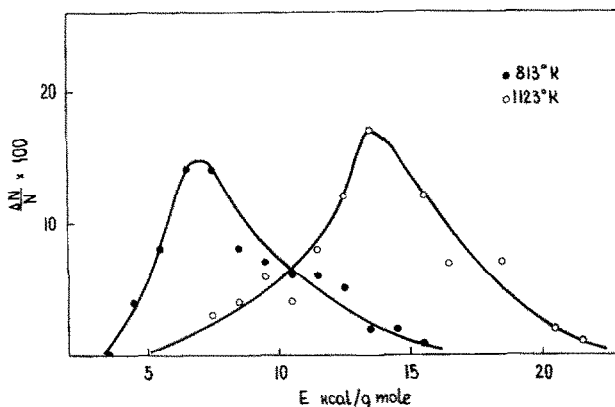


FIG. 4. Distribution curves of active centers with respect to the corresponding activation energies for silver plates treated at 813° and 1123°K.

from 4.5 to 11 kcal/g mole, a minimum being observed for plates heated at 723–773°K. A plate was first heated at 1123°K and then treated in vacuum at 393°K. In the course of evacuation its activity increased at first, reached a maximum and then decreased, reaching practically full deactivation. This effect is connected with the removal of oxygen from the surface and from the bulk of silver and with the participation of oxygen in the formation of some active centers on the surface (13). It is interesting to establish the activation energy distribution of the active centers for different temperatures of treatment of silver as well as to establish whether the changes in the rate constant values provoked by evacuation are due to changes in the activation energy, or to changes in the number of active centers on the surface.

Figure 4 shows the distribution curves giving the number of bubbles corresponding to a given activation energy value (in an interval of 1 kcal/g mole) for plates treated at 813° and 1123°K. It is seen that the surface is heterogeneous and contains active centers showing a large range of activation energy values. But the greater part of these centers have energies of activation corresponding to the values determined by Bliznakov and Peshev (7 and 13.5 kcal/g mole, respectively).

Figure 5 shows the change in the most probable value of activation energy, depending on the time of evacuation of the

silver plate at 633°K. It is evident that the activation energy first decreases and then increases smoothly, reaching a constant value of 15 kcal/g mole. Simultaneously a considerable change in the number of bubbles is observed. This number increases at first, passes through a maximum and then decreases, continuously tending towards zero. The results show that the activity of the silver plate changes upon treatment under vacuum due to changes in both the activation energy and the number of the active centers. The centers containing most strongly bound oxygen have the greatest activation energy.

If a plate deactivated by vacuum treatment is allowed to stay in diluted peroxide

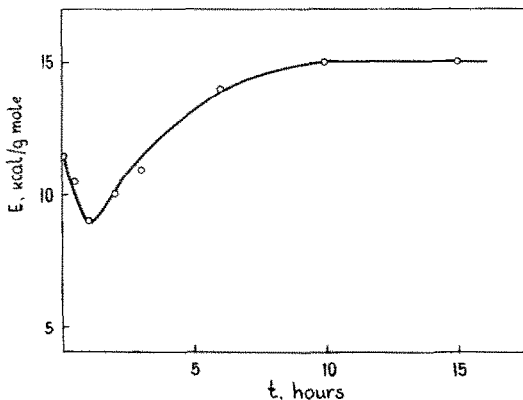


FIG. 5. The change in the activation energy of a silver plate depending on the duration of thermal treatment in vacuum.

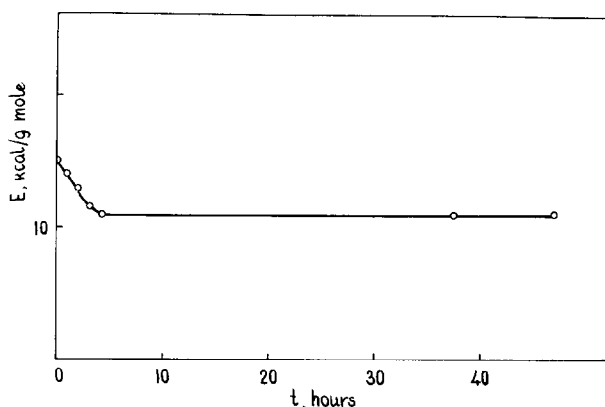


FIG. 6. The change in the activation energy of a silver plate deactivated in vacuum and then allowed to stay in hydrogen peroxide solution.

solution its activity gradually increases. As is seen from the data shown on Fig. 6, the activation energy of the process gradually decreases and tends towards 11 kcal/g mole this value being characteristic for the plate, before vacuum treatment. According to Roginsky the mechanism of decomposition of hydrogen peroxide on catalysts which are electron conductors requires the participation of at least two kinds of active sites: electron donors and acceptors (14). This mechanism was proved indirectly in other investigations of ours (15, 16). Most probably, the oxygen takes part in the formation of one type of center or in the formation of centers with different potentials. Since a pair of such centers acts as a microgalvanic element, the removal of oxygen from the

surface leads to full deactivation of the silver. The above results show once more the role of oxygen in the formation of active centers on the silver catalyst surface.

The distribution curves of active centers with respect to the corresponding activation energy for the faces (100) and (211) of a silver single crystal are given on Fig. 7. The existence of such distributions on the individual faces is evident. However, the most probable values of the activation energy differ considerably. The face (100), being more closely packed, has a lower activation energy than (211). Rienäcker and Völter (6) obtain a similar result in the case of the decomposition of formic acid on a copper single crystal, comparing the average activities of faces (111) and (100).

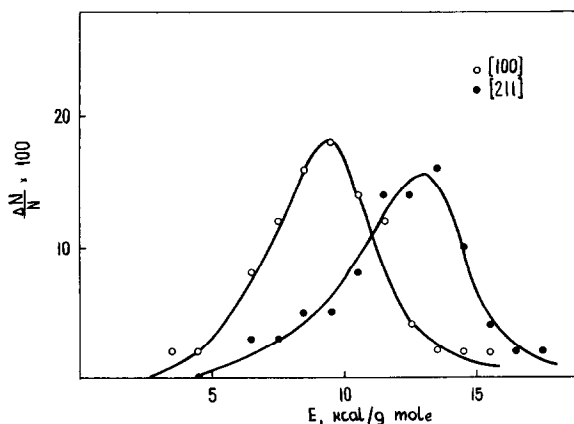


FIG. 7. Curves of distribution of active centers with respect to their activation energy for different types of faces of a silver single crystal.

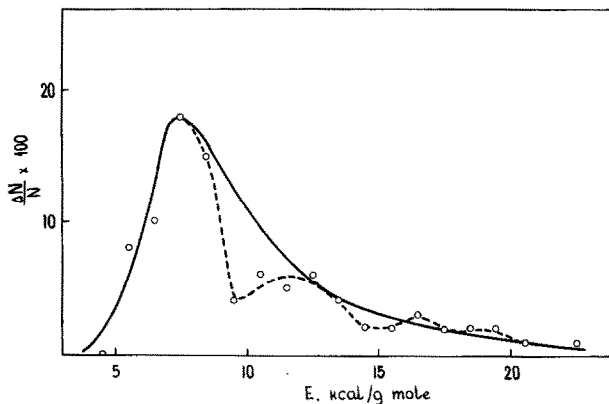


FIG. 8. Distribution curve of active centers with respect to energy of activation on the surface of a gold plate.

It must also be mentioned that the number of bubbles appearing on the (100) face is considerably smaller than the number corresponding to the (211) face.

It is of interest to obtain comparative experimental data on the catalytic activity of copper, silver, and gold with respect to the reaction under consideration.

It was established that on the gold surface there are active centers whose activation energy lies within the range of 5–25 kcal/g mole. As is seen from Fig. 8, the most probable value of the activation energy is about 7.5 kcal/g mole. The distribution spectrum exhibits also a fine structure with maxima in the range of larger activation energy values.

Figure 9 shows the distribution curve obtained in the case of decomposition of hydrogen peroxide on the surface of copper. The maximum corresponds to an activation energy of about 6.5 kcal/g mole.

It must be pointed out that the most probable activation energy values obtained with both metals are small and close to the value corresponding to silver plates treated at lower temperatures (7.0 kcal/g mole). Such close values for the three metals confirm the role of the electron factor in catalysis. The three metals have similar electron configurations, the same *d* characteristics (36%) and equal work functions (4.3 eV). It must be pointed out too that irrespective of the modification of the surface accom-

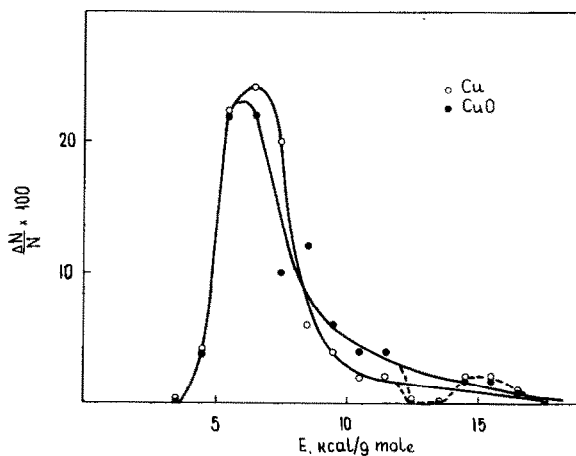


FIG. 9. Curves of distribution of active centers with respect to activation energy on the surfaces of copper and copper monoxide.

panying the peroxide decomposition and the oxygen evolution, the most probable values of the energy of activation are comparatively close to each other.

In all cases studied the peroxide decomposition is preceded by a latent period. The bubbles do not appear at the beginning, but after a period of about 10 min, the whole process being observed for about 40–50 min. The presence of such a latent period may be due to saturation of the surface with oxygen. In this connection it was necessary to obtain data concerning the activity of a metal plate with previously oxidized surface and to compare this activity with the data obtained with pure copper. For this purpose, copper plates were heated in the air at 1173°K for 3 hr. The plates became black due to the formation of copper monoxide. The distribution curve given in Fig. 9 shows that the activity of copper monoxide is almost the same as that of the pure copper plate. The distribution curves are similar even in their fine structure. This leads to the conclusion that in the case under consideration the activity of the metal copper plate is in fact the activity of the oxide formed on the surface. It can be noticed too that the work function of the monoxide surface is very close to that of pure copper (4.35 eV).

CONCLUSIONS

On the basis of the present experimental investigation it may be concluded that the surface of the investigated catalyst is heterogeneous. The distribution curves obtained show that on both polycrystalline and single-crystal surfaces there are active centers having different activation energies. The most probable values for the activation energy are different for different crystal faces. More closely packed faces show lower activation energy.

For the metals of the copper group the prevailing number of active centers have close activation energies. This is evidence for the influence of the electron structure on the catalytic properties of metals.

The metal surface is modified by the oxygen evolved during the reaction. It has

been confirmed that the active centers are formed on the surface with the participation of oxygen.

The activity of the silver catalyst changes considerably under the effect of oxygen. The activation energy of the processes taking place on silver surfaces may vary in a large range (from 6 to 15 kcal/g mole) depending on the oxygen content. The change in the latter may be produced by heating silver plates in air or under vacuum.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Miss Leila Georgieva, Miss Fimka Misheva, and Mrs. Mariana Konstantinova, who took part in the various stages of the experiments.

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