

NOTES

The Decomposition of Hydrogen Peroxide on Variously Treated Copper Foils

Many attempts have been made to establish the relationship between surface emergent defects in solids and their catalytic activity; this is because it is thought that the activity of a heterogeneous catalyst resides chiefly at the interface between the solid catalyst and the reacting species. The interface is considered to lower the potential energy barrier between reactants and products by activating the reactants and by increasing the probability of formation of a transition state. Hence, a change in the surface properties of a metal would be expected to effect its efficiency as a catalyst.

Conflicting results have been found in this field; the first, by Eckell (1), which was later interpreted by Cratty and Granato (2), showed that the catalytic activity of nickel sheet for the hydrogenation of ethylene depended upon the state of the catalyst—with respect to rolling and annealing.

Krause and Hermann (3), and later Keating, Rozner, and Youngblood (4) have shown that the deformation of platinum foil increases its catalytic activity.

On the other hand Bagg and co-workers (5), studying thin silver films amenable to transmission electron microscopy, and more recently Jaeger (6) studying silver crystals, showed that the concentration of surface emergent defects had no effect on their catalytic activity in the decomposition of formic acid at 180° and 260°C.

Uhara and his colleagues (7-11) have studied the activity and subsequent effects of annealing on cold-worked copper and nickel wires. In the case of cold-worked

copper wires catalyzing the decomposition of benzene diazonium chloride, an abrupt decrease in activity occurred for the annealing range 300-430°C. There was also a concurrent change in hardness (12) and the loss in catalytic activity was attributed to a decrease in point defect concentration over this temperature range. In the present study we have made similar experiments for the hydrogen peroxide decomposition on metal foils, our main point being to use a high-vacuum technique which excludes tap grease and other contaminants from the system.

EXPERIMENTAL

The increase in pressure was measured by a transducer incorporated in an all glass system; a full description of the apparatus will be given in a later publication.

Copper foils. The foils were prepared from Grade I Copper Sheet (Johnson Matthey & Co. Ltd., 0.254 mm thick). This was then rolled to 0.190 mm and 0.127 mm thickness in a precision cold-rolling mill in Nottingham University's Metallurgy Department; according to the mill operators there was no possibility of the surface being affected by foreign metal pick-up.

Hydrogen peroxide. The hydrogen peroxide used was prepared from a sample of 86% w/w unstabilized H. T. P. kindly supplied by Laporte Chemicals Ltd., Luton. This solution was then diluted to 6% as required; 6% was chosen as this appeared to give the optimum reaction rate. The solution strength was checked periodically by titration with acidified potassium permanganate.

RESULTS

The dependence of reaction velocity, v , on annealing temperature is shown in Fig. 1; this result is similar to those obtained by Uhara and co-workers (7) on benzene dia-

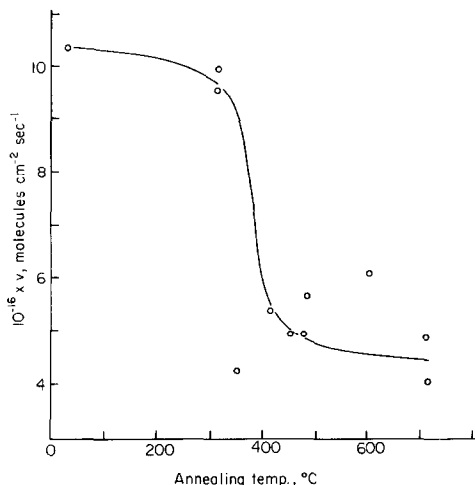


FIG. 1. The effect of annealing temperature on the catalytic activity for H_2O_2 decomposition of cold-worked Cu foil.

zonium chloride decomposition. Several attempts were made to etch for dislocations but these proved singularly unsuccessful. An explanation for this can be found in the work of Young (13), who showed that

etchants for copper are specific to a given crystal face.

The rate of decomposition on the foils of different thickness is shown in Fig. 2; the order of reactivity is $0.127 \text{ mm} > 0.19 \text{ mm} > 0.254 \text{ mm}$, i.e., increases with the amount of rolling work done on the foil.

When the copper foil was suspended in hydrogen peroxide it was observed that, after an initial induction period, reaction appeared to be coming from the solution, as well as the copper surface. A photographic comparison with the decomposition on gold which was found to be entirely heterogeneous is afforded by Figs. 3(a) and 3(b). During a series of experiments the foil was withdrawn from the solution at the end of the induction period without disturbing the reaction system; the reaction then continued as instanced in Fig. 4. This demonstrates the presence of a homogeneous decomposition caused by dissolved copper ions.

Activation energies and frequency factors were also determined for variously annealed 0.127-mm foils; there was found to be no relationship between either activation energy, E , or frequency factor, A , and annealing temperature, although a compensation effect was found (Fig. 5). The equation for this was found to be

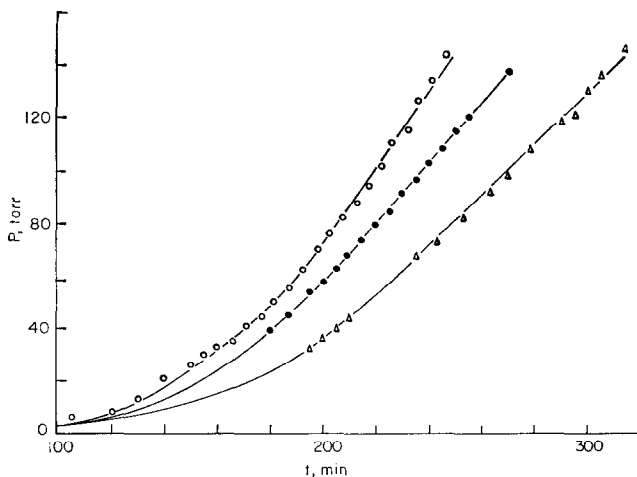


FIG. 2. The effect of increased cold-work on catalyst activity. The thinner foils are the more cold-worked; Δ , 0.254 mm; \bullet , 0.190 mm; \circ , 0.127 mm.

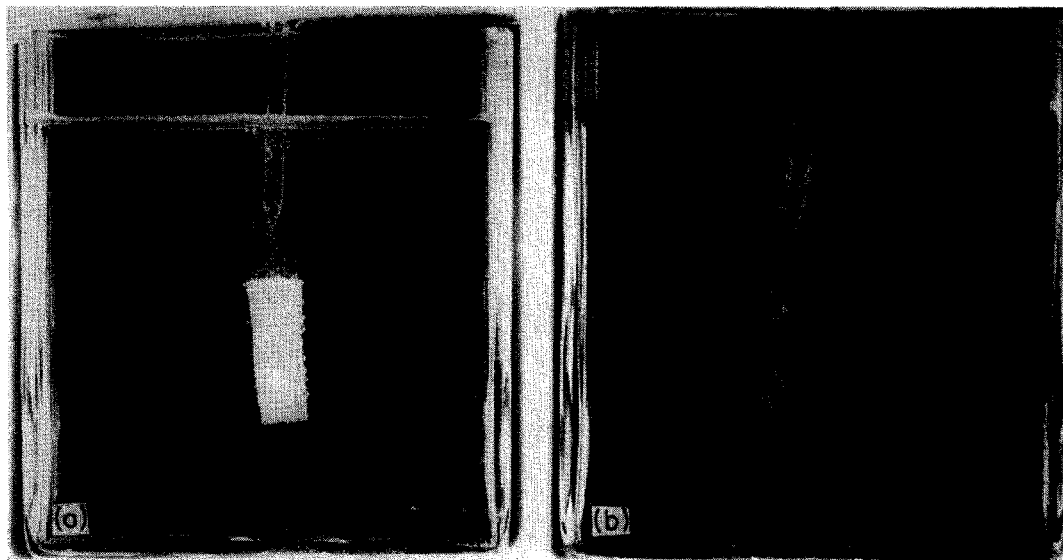


FIG. 3. To show how the oxygen bubbles come only off the gold surface (a), while for copper they come from the surface of the metal, and also from the solution (b).

$$\log_{10} A = 0.668E + 17.2$$

for which the standard deviation $\sigma = 0.012$.

Blank reactions were carried out on the reaction vessel alone, but as the rate of decomposition was only about 1% of that on copper, the effect of this was disregarded.

The results on glass are summarized in the table.

$10^{-12} \times v$ (molecules $\text{cm}^{-2} \text{sec}^{-1}$)	E (kcal mole $^{-1}$)	$\log_{10} A$ (molecules $\text{cm}^{-2} \text{sec}^{-1}$)	
7.8	19.9	28.4	
9.9	18.9	27.8	
9.3	20.4	28.9	
5.7	18.4	27.3	
Average values	8.2	19.4	28.1

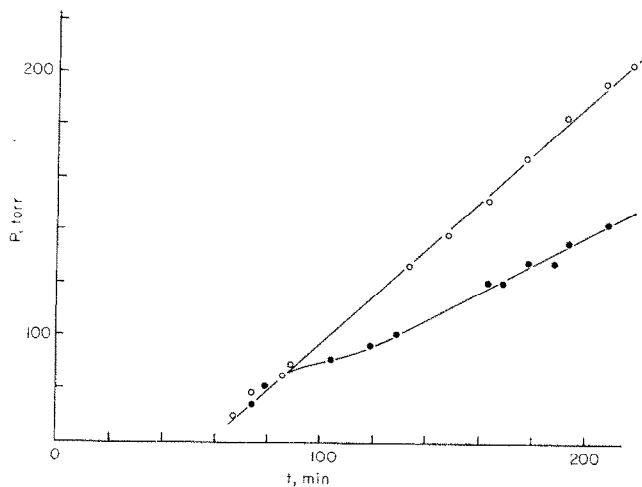


FIG. 4. To show how the reaction continues at a reduced rate when the foil is removed from the H_2O_2 solution. Foil immersed for all the reaction (\odot), foil removed after 90 minutes (\bullet).

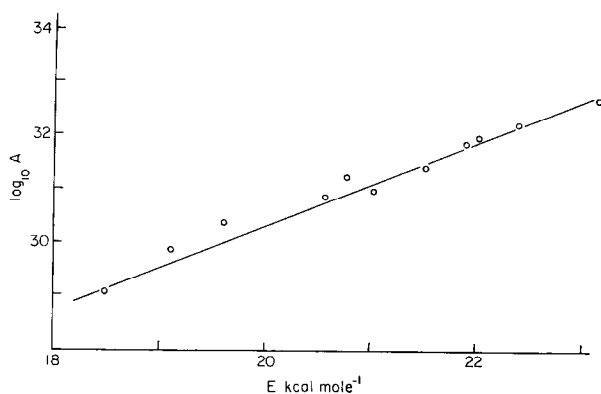


Fig. 5. The compensation effect of H_2O_2 decomposition catalyzed by copper foils.

DISCUSSION

Our results quantitatively confirm the work of Uhara and co-workers. We would, however, offer a possible alternative interpretation. Young (14) has shown that for oxide formation on copper single crystals there is no correlation between oxide nuclei and dislocations. Preferential oxidation on certain single-crystal faces has also been well established; this leads us to the conclusion that it is the surface structure (that is, the orientation of crystallites in the metal surface) which is the important factor, and not the defect or dislocation structure. The effect of annealing will be to decrease but not completely remove the active lattice planes, leaving a residual reaction velocity. The effect of increased rolling introduces some degree of structure into the metal and the proportion of active crystallite faces at the surface is proportional to the degree of cold-working.

Our demonstration that the copper-catalyzed reaction is both homogeneous and heterogeneous is in direct contrast to the results of Dowden and Reynolds (15). This discrepancy can probably be explained by the time of reaction used in their experiments, which was too short to allow appreciable solution of ions to occur.

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