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The Activity of Abraded Copper/Copper Oxide Foils in Heterogeneous Catalysis

It has been claimed (*1, 2*) in recent years that the activity of metal oxides in heterogeneous catalytic reactions may be understood better by applying the newer theories of inorganic complex formation to those processes occurring at a surface. This is in contrast to relating activity patterns to properties of oxides as semiconductors in terms of the band theory of solids (*3*). In both of these approaches, however, attention has to be given to the chemical and mechanical nature of the surface. In particular, the influence of Volkenshtein's micro- and macroscopic defects (*4*) have to be considered.

In this investigation the activity of "Specpure" copper foils (6 cm × 3 cm × 0.1 mm thick), initially supporting air-grown oxide films, was examined in the decomposition of hydrogen peroxide vapor. A comparison was sought for the performance of cuprous oxide films supported on (a) smooth and (b) abraded copper surfaces. The flow apparatus, metal foil reactor and experimental technique adopted have been described previously (*5*). The steady activity level was determined at each point in the temperature cycle 80°–60°–100°–40°. Abrasions were introduced by scratching the foils carefully with a sharp corner of the same material along a straight edge. Prior to exposure to H_2O_2 vapor both smooth and abraded foils were annealed in air for 45 min at 80°.

Figure 1 shows the variation of activity (as percentage decomposition) with time in achieving the steady level. In general smooth foils attained this level after 40 min exposure. At 100°, the initial fall and then rise in activity of the lower temperatures was not detected. This is consistent with earlier findings using "Specpure" slips (*5*), and may be connected with the growth of an oxide film on the metal.

The effect of abrasion on activity is shown also in Fig. 1, for foils scratched 6 cm in length and ca. 0.1 mm in width along two diagonals. A surprising increase in activity was detected, most pronounced at the lower temperatures. On first exposure to H_2O_2 vapor some cyclic activity variation was noted and the first steady level at 80° was not achieved before 90–100 min exposure. Subsequent runs settled to the same steady level in 40 min, and no deterioration in activity was detected after standing the foils in air at room temperature for three days.

Foils were abraded further by 3 parallel scratches, 6 cm long spaced 0.5 cm, crossing the diagonals. Little or no further improvement was detected with these specimens. Thus at 80°, diagonally abraded foils gave 87% decomposition which increased only to 88.6% on further treatment.

In Fig. 2, Arrhenius plots of first order rate constants are shown for (a) smooth and (b) abraded foils. These plots gave

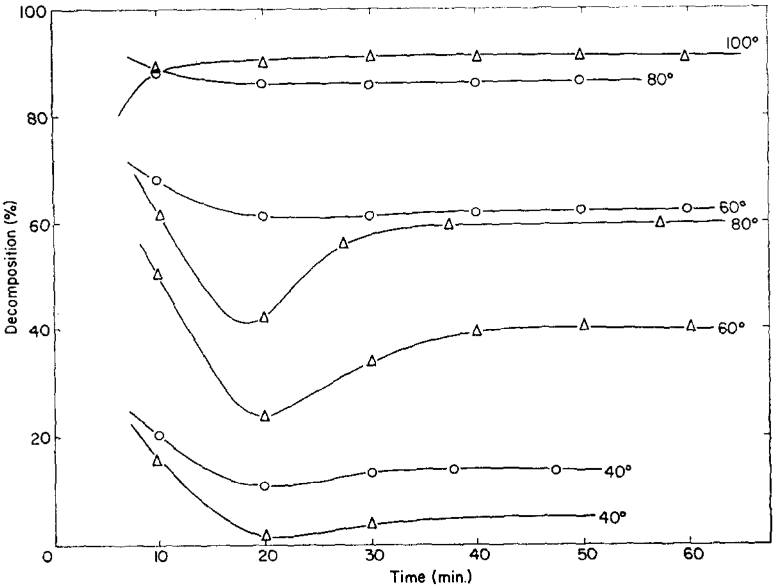

FIG. 1. Initial decomposition patterns (p.p. $H_2O_2 = 1$ mm Hg); △, smooth foils; ○, diagonally abraded foils.

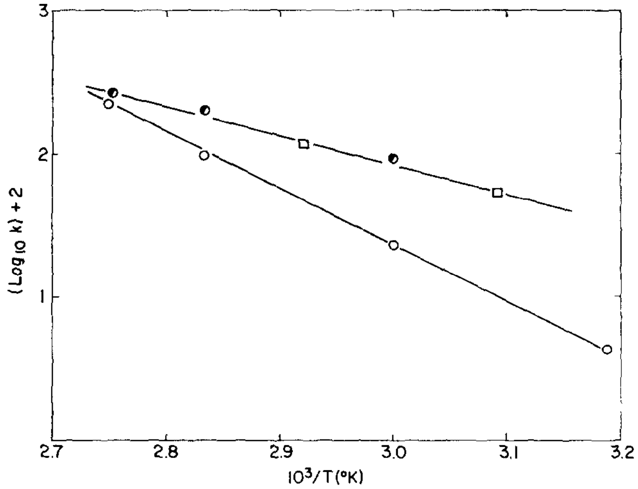

FIG. 2. Arrhenius plots of first order rate constants; ○, smooth surfaces; ◐, diagonally abraded surfaces; □, multiply abraded surfaces.

18.4 kcal/mole for (a) and 9.2 kcal/mole for (b). The value for (a) is the same as that for bulk CuO (*5*) but higher than that found previously for Cu_2O/Cu slips.

The foils weighed 1.2–1.3 g but it was not found possible to measure the surface area of each by krypton adsorption. Three foils had to be bulked together to make the surface area appreciably larger than that of the sample tube. The approximate value found was 35 cm^2/g which gave a roughness factor of 1.2. However, the experimental error in these measurements could be as high as 50% as indicated by an examination of the experimental data without regard to the known geometric area. Hence no real difference in the surface area of the smooth and abraded foils could be detected with this technique. In any case, the abrasions covered so small a geometric area as compared to the whole surface that the activity improvement could not possibly be attributed to an area effect alone.

Surfaces were examined by etching with solutions designed to reveal dislocation sites by surface pits in the copper foils (*6, 7*). The best method found was to treat with $4M$ HNO_3 for 5–10 sec followed by 30 sec in an $FeCl_3HBr$ mixture (*7*). While smooth foils showed only characteristic grain structure, abraded surfaces showed several triangular etch pits lying along the diagonal abrasions, and, in one example, pits were noted lying perpendicular to the diagonals. The etch pit density was low (ca. 1 per cm length of abrasion), but could be considered typical in shape to that expected from pits at edge dislocations on a (111) face (*7*). It is impossible to be absolutely certain about this as the foil surfaces were not specifically oriented and probably were multi-facial. Nevertheless, it is believed that these experiments demonstrate in a simple manner that a relationship exists between catalyst activity and the "mechanical" condition of the supporting surface. Previously such comparisons have been implied only in studies of activity variations with irradiated materials (*6*).

This work is now being extended to include an examination of cuprous oxide film supported on crystal faces of high-purity copper grown from the melt. I am indebted to Dr. D. Shooter, I.C.I., H.O.C. Division for the surface area data.

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