Mobility of Copper Metal During Heterogeneous Catalytic Decomposition of Formic Acid

Although there have been several mechanistic studies of the heterogeneous catalytic decomposition of formic acid on copper (*1*), it would appear that the occurrence of sublimation, sintering and surface retexturing of the metal has not previously been described and discussed. Such behavior is not unexpected since it has long been known that copper forms mobile and/or volatile compounds [e.g., Ref. (*2*)]; the sublimation of metal which accompanies the decomposition of copper(II) formate (*3–5*) is of particular relevance here. In a recent kinetic and mechanistic investigation of the solid-phase decomposition of copper(II) formate, between 432 and 506 K, we ascribed (*6*) the sublimation of copper during reaction, the sintered appearance of the residual product and certain kinetic features of the reaction to the formation of a volatile and very unstable intermediate, probably copper(I) formate (*4, 7*). Similarities of observed behavior led us to conclude that either copper formate is an intermediate in the heterogeneous rate process on copper [a general reaction mechanism which has been extensively debated in the literature (*8*)] or that both heterogeneous and solid-phase reactions involved the formation of a common volatile intermediate.

Morphological changes of a copper powder catalyst, which occurred during the heterogeneous decomposition of formic acid, were studied using a flow system. A stream of pure nitrogen (~10 Torr) was passed through a 10 mm plug of copper powder (electrolytic, <200 mesh to dust) confined in a glass tube with glass wool. When the catalyst had been heated to reaction temperature (450–500 K) the gas flow was deflected to pass through a bubbler containing formic acid (Analar, 90%, at 290 K) for ~30 min. The stream of pure nitrogen was then restored and the catalyst was cooled. Following the catalytic reaction the following changes were observed.

i. Sublimation. Reaction resulted in the formation of a copper mirror on the walls of the reaction vessel in the immediate vicinity of the metal powder. The maximum displacement of the sublimate from the metal was always small (<1 mm) so that the edge of the adherent mirror faithfully recorded the outline of the region occupied by the catalyst. Sublimation was detected only when a clean glass tube was used, and deposition was apparently prevented by contaminants, such as silicone grease, on the walls of the vessel. The maximum distance of diffusion of the sublimed metal was similar to that observed during decomposition of copper(II) formate, evidence strongly indicative of the participation of the same intermediate in both reactions.

ii. Sintering. The catalytic process resulted in some sintering of the active metal. The copper catalyst was introduced into the reaction vessel as a freely flowing powder but was subsequently withdrawn in the form of a coherent plug comprised of a mechanically weak aggregate of the metallic particles.

iii. Surface texture. The heterogeneous reaction also resulted in textural changes of the copper powder. This is seen from comparison of typical "Stereoscan" photographs of particles of copper as supplied (Fig. 1) and after participation in the catalytic reaction (Fig. 2). An increase in surface roughness which resulted from reaction was also apparent by examination of electron micrographs for replicated surfaces. The size of the small protuberences which were present on the metal surfaces after reaction (~0.5 μm diameter) is comparable with a preferred particle size (~0.3

FIG. 1. The unused copper powder, as supplied; ×1300.

μm) of the product from decomposition of copper(II) formate (*6*): this is a further point of similarity between the two reactions.

This mobility of the metal is ascribed to the formation of a volatile, but very unstable intermediate which is identified as copper(I) formate. It has been shown that copper(I) formate can be volatilized, possibly as polymeric species, but the compound is so unstable that it is difficult to obtain an acceptable mass spectrum (*9*). These properties fulfill the requirements expected of the intermediate postulated in the catalytic reaction, and, in the absence of a probable alternative, we identify copper(I) formate as the mobile participant in the heterogeneous process. Moreover, the observed similarities (i.e., metal sublimation and sintering) between the catalytic decomposition of formic acid and the solid-phase reaction of copper(II) formate can be

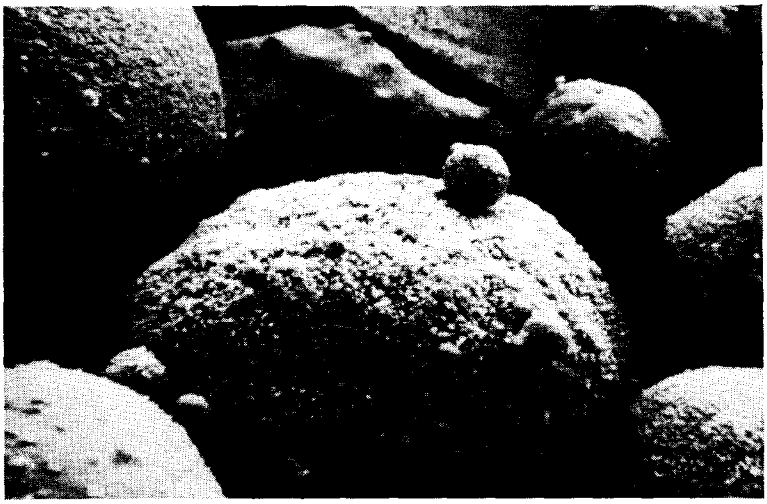

FIG. 2. Representative examples of the texture of the surfaces of particles of copper powder after useas a catalyst for decomposition of formic acid; ×1300.

ascribed to the involvement of the same intermediate (*6, 7*) in the latter rate process.

The possibility of surface reorganization during heterogeneous catalytic reactions is not a new concept. Where there are progressive changes of the effective active area during reaction it may be necessary to make due allowance for such variation in the interpretation of kinetic data. To express an Arrhenius pre-exponential factor (A) in units (molecules $area^{-1}$ time^{-1}) systematic changes of area due to sublimation, sintering and surface retexturing during reaction may require consideration. Progressive changes of area could also influence the apparent activation energy (E). As discussed elsewhere (*10*), a series of comparable reactions, in which the temperature dependencies of the concentrations of the precursors to product formation are different, exhibit compensation between A and E. Such variations may be expected in different studies of the present heterogeneous reaction since (i) the rate of change of catalyst area, and (ii) the lifetimes, the concentrations and rates of decomposition of the volatile intermediates may be influenced by (inter alia) the particle sizes and the distribution of the metal catalyst and the pressures of gases present. This model, therefore, theoretically accounts for the well-known (*1*) compensation behavior observed for the decomposition of formic acid on copper. The catalytic reaction proceeds in the temperature range of copper formate instability and both A and E are sensitive to changes in concentration of the intermediates for which the lifetime is dependent on experimental conditions.

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REFERENCES

1. BOND, G. C., "Catalysis by Metals," p. 420. Academic Press, London, 1962.
2. BLOOM, H., *Nature (London)* **159**, 539 (1947).
3. KÖRÖSY, F., *Nature (London)* **160**, 21, (1947).
4. KELLER, A., AND KÖRÖSY, F., *Nature (London)* **162**, 580 (1948).
5. BECUE, C., *Bull. Soc. Chim. Fr.* 564 (1950).
6. BROWN, M. E., GALWEY, A. K., AND JAMIESON, D. M., unpublished data.
7. SCHUFFENECKER, R., TRAMBOUZE, Y., AND PRETTRE, M., *Ann. Chim. (Paris)* **7**, 127, 133 (1962).
8. TRILLO, J. M., MUNUERA, G., AND CRIADO, J. M., *Catal. Rev.* **7**, 51 (1972).
9. EDWARDS, D. A., AND RICHARDS, R., *Inorg. Nucl. Chem. Lett.* **8**, 783 (1972).
10. WILSON, M. C., AND GALWEY, A. K., *Nature (London)* **243**, 402 (1973).

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