

## The Importance of Defects in Nickel on the Catalytic Dehydrogenation of Formic Acid at Low Pressures

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FORMIC ACID at a pressure of  $5 \times 10^{-5}$  torr was catalytically decomposed on heated nickel wires (Grade 1, Johnson Matthey), in an ultra-high vacuum flow system.<sup>1</sup> Flashing the wire in a vacuum increased its activity by several orders of magnitude; the initial reaction probability,  $P$ ,

varied from 0.2 at 200° to almost unity at temperatures as low as 500°. During the reaction some decay in activity occurred. The rate of decay was dependent on the type of vacuum system used, the previous history of the wire, and the formic acid reactant pressure.

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The possibility existed that "catalytic super-activity" of a wire was attributable to a high defect content introduced into the wire by the act of flashing and radiation quenching; such a theory was considered by Duell and Robertson<sup>2</sup> for copper and nickel wires. The theory appeared to receive support from the fact that the absolute activities observed by Sachtler and Fahrenfort<sup>3</sup> on unflashed nickel surfaces were about 300 times less at 200°.

If the decay in catalytic activity could be correlated with the annealing-out of crystallographic defects such as vacancies and dislocations introduced into the lattice of the nickel wire as a result of flashing, then it should be possible to induce extra activity into the wire by torsionally deforming it. Similarly, by twisting a wire during the reaction while maintaining a constant heating current, a decay in the catalytic activity might be prevented from occurring.

Cold-working nickel leads to the defect energy being stored as dislocations and vacancies.<sup>4</sup> The dislocation density rises with the amount of strain imposed on the metal and corresponds to  $10^6$ – $10^8$  cm.<sup>-2</sup> for non-deformed metals and to  $10^{11}$  cm.<sup>-2</sup> for heavily worked metals; saturation occurs at about  $10^{12}$  cm.<sup>-2</sup>.<sup>5</sup>

An all-metal reaction chamber (base pressure  $< 5 \times 10^{-9}$  torr) was constructed and used in place of the glass system. The dehydrogenation of formic acid was followed by continuously monitoring the hydrogen peak with a mass spectrometer and penchart recorder. The catalyst could be twisted with the aid of a rotary-motion drive.

Formic acid was decomposed on nickel wires which had been thoroughly outgassed at temperatures close to the melting point and then annealed in vacuum. No decrease in activity occurred during the annealing treatment. Rapid twisting of a wire during reaction had no effect on its absolute activity. Decay of activity occurred regardless of whether the wire was being twisted, even when twisted to the point of fracture (173 turns, 4.5 cm. in length and 150  $\mu$ m diameter wire).

Two significant points emerged from these experiments; (a) decay of activity occurred while the catalyst was being worked and (b) the decayed activity could not be recovered by saturating the metal lattice with defects. It appears, therefore, that the loss of activity during reaction is due to progressive contamination of the surface by products of reaction (*e.g.* carbon deposition), and that defects are not important in determining the absolute activity of a wire.

Loss of activity by platinum as a result of carburisation during formic acid decomposition in a conventional vacuum has already been discussed.<sup>6</sup> An important difference between platinum and nickel is that with the latter, the superactive state could not be produced by prolonged exposure of the wire at dull red-heat to hydrogen. Flashing the nickel had the effect of producing a considerably less contaminated and thence catalytically super-active surface.

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<sup>2</sup> M. J. Duell and A. J. B. Robertson, *Trans. Faraday Soc.*, 1961, **57**, 1416.

<sup>3</sup> P. Mars, J. J. F. Scholton, and P. Zwietering, *Adv. Catalysis*, 1963, **13**, pp. 54–56.

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<sup>5</sup> P. B. Hirsch, *Progr. Metal Phys.*, 1957, **6**, 236.

<sup>6</sup> E. M. A. Willhoft and A. J. B. Robertson, *J. Catalysis*, in the press.