

Sinfelt J H, Carter J L & Yates D J C. Catalytic hydrogenolysis and dehydrogenation over copper-nickel alloys. *J. Catalysis* 24:283-96, 1972.  
[Corporate Research Laboratories, Esso Research and Engineering Company, Linden, NJ]

As catalysts, copper-nickel alloys are less active than pure nickel by orders of magnitude for hydrogenolysis of ethane to methane, but are severalfold more active for dehydrogenation of cyclohexane to benzene. Thus, the effects of alloying depend strongly on the nature of the reaction. [The *SCI*<sup>®</sup> indicates that this paper has been cited in over 250 publications.]

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Shortly after World War II, scientists became interested in using metal alloys as catalysts to probe the relationship between the catalytic activity of a metal and its electronic structure.<sup>1,2</sup> Alloys consisting of one metal from Group VIII and another from Group IB of the periodic table, e.g., nickel-copper, were of particular interest.<sup>3</sup> Emphasis was given to a few selected reactions, one of which was the hydrogenation of ethylene. Little or no attention was given to hydrogenolysis reactions of hydrocarbons, which involve scission of carbon-carbon bonds. The possibility that the effect of alloy composition on catalytic activity for this type of reaction could be very different from the effect for hydrogenation (or dehydrogenation) reactions was not appreciated, nor was the selectivity aspect of catalysis by metal alloys in general much appreciated. Results of research addressing this issue led to the paper that is the subject of this commentary.

The research was conducted in the Corporate Research Laboratories of Exxon (then Esso) Research and Engineering Company as part of a comprehensive program on bimetallic catalysts that I initiated in the early 1960s. Measurements were made of rates of hydrogenolysis of ethane to methane and of dehydrogenation of cyclohexane to benzene on copper-nickel alloys of different compositions. D.J.C. Yates contributed adsorption data for determination of the surface areas of the alloys and for providing an approximate measure of their surface compositions. J.L. Carter and I worked together in obtaining the cyclohexane dehydrogenation data, while I was responsible for obtaining the ethane hydrogenolysis data.

The copper-nickel alloys were less active than pure nickel by orders of magnitude for ethane hydrogenolysis. However, they were severalfold more active for cyclohexane dehydrogenation, despite the fact that pure copper is much less active than pure nickel for the reaction. The results showed clearly that the effect of copper on the catalytic activity of nickel is very different for the two reactions, and that selectivity is therefore an important aspect of catalysis by this type of alloy. Prior to publication of this paper, we had disclosed selectivity effects in several patents on alloy catalysts comprising combinations of metals from Groups VIII and IB.<sup>4,5</sup>

I believe that the many citations to this paper are due to its role in stimulating widespread interest in the selectivity phenomenon in catalysis by alloys and in reviving an interest in bimetallic catalysts in general. In the time that has elapsed since the publication of our work on copper-nickel alloys in 1972, there has been much scientific progress in this field. Major technological advances have also been achieved, a prime example of which is the application of bimetallic catalysts in petroleum reforming processes. Both the scientific and technological aspects are considered in a recent monograph.<sup>6</sup>

1. Schwab G M. Alloy catalysts in dehydrogenation. *Discuss. Faraday Soc.* 8:166-71, 1950. (Cited 70 times since 1955.)
2. Dowden D A & Reynolds P. Some reactions over alloy catalysts. *Discuss. Faraday Soc.* 8:184-90, 1950. (Cited 80 times since 1955.)
3. Best R J & Russell W W. Nickel, copper and some of their alloys as catalysts for ethylene hydrogenation. *J. Amer. Chem. Soc.* 76:838-42, 1954. (Cited 85 times since 1955.)
4. Sinfelt J H, Barnett A E & Dembinski G W. *Isomerization process utilizing a gold-palladium alloy in the catalyst.* US patent 3,442,973. 6 May 1969.
5. Sinfelt J H, Barnett A E & Carter J L. *Inhibition of hydrogenolysis.* US patent 3,617,518. 2 November 1971.
6. Sinfelt J H. *Bimetallic catalysts: discoveries, concepts, and applications.* New York: Wiley, 1983. 164 p. (Cited 60 times.)

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