

We know that zinc oxide, magnesium oxide, titanium dioxide and lead oxide (yellow) are *n*-type semiconductors and when the hydrazine is adsorbed on them the *F*-centres on these surfaces may be occupied by hydrogen atoms from the hydrazine. The radical which develops is resonance stabilized and the surface helps to maintain its planarity. Later, when one of the *o*-nitro groups picks up the hydrogen the hydrazine eliminates a water molecule and the nitrosoazo-compound is obtained. The *F*-centres on the surface are easily quenched by water or acids and the reaction therefore ceases. The mineral acids also inhibit the acidic nature of the hydrazine. On basic oxides such as zinc or magnesium oxide, the anion which develops in solution on adsorption turns into the radical, hence the end product is the nitrosoazo-compound. On easily reducible oxides such as mercuric oxide (yellow) or lead dioxide and *p*-type oxides such as copper oxide or lead oxide (red), such a mechanism obviously cannot take place and 2,4,6-trinitroazobenzene is obtained by a simple oxidation mechanism.

This work was supported by a grant from the US National Science Foundation.

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Received March 21, 1967.

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### An Unusual Activity Pattern in Hydrogen-reduced Nickel-Copper Alloy Catalysts

STUDIES with binary alloys have often been used in efforts to define the electronic factor in catalysis, and special interest has been attached to the compositions at which breaks in the activity occur. Frequently, however, measured patterns of activity cannot readily be related to changes in the electronic structure of the metal<sup>1</sup>. This communication reports that after sustained hydrogen reduction homogeneous samples of "mixed" evaporated films of nickel and copper exhibit a surface the composition of which is insensitive to the bulk composition. Because preliminary hydrogen-reduction is frequently practised in basic studies we would like to emphasize that the extent to which measured activities are affected probably depends on the duration of such reduction.

Nickel-copper films (80–120  $\mu\text{g}/\text{cm}^2$ ) were prepared by vacuum evaporation in 'Pyrex' bulbs. Reduction of the metal deposit for 2 h at 530° C was followed by cooling to -95° C and evacuation for 10 min. It was ascertained that the "mixed" films were homogeneous by diffractometer profiles of the Debye-Scherrer reflexions. Reaction of a standard 8:1 hydrogen/butene-1 mixture (total pressure 1.0 mm) on a series of films gave the activity pattern shown in Fig. 1. Because the areas of the films were similar, the specific activities were similar for pure nickel and for alloys containing as little as 6.3 atom-per cent nickel.

Sachtler and Dorgelo<sup>2</sup> have reported phase separation (which is favoured thermochemically) in the nickel-copper system when atom transport is made possible by high surface/volume ratio, as in evaporated films. Such separation would give phases of typical nickel content

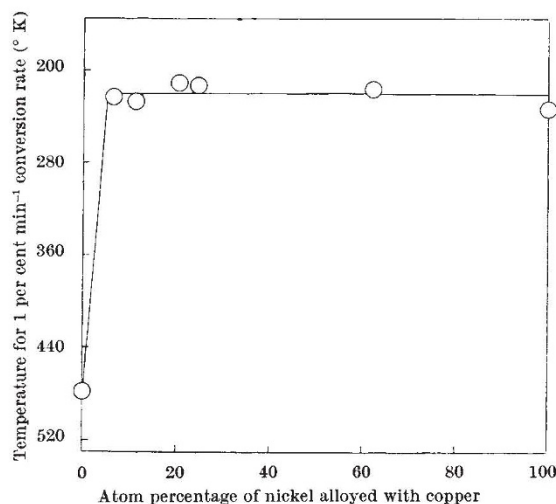


Fig. 1. The hydrogenation of butene-1 over nickel-copper alloy films: activity pattern.

98 per cent ( $\alpha_1$ ) and 20 per cent ( $\alpha_2$ ). The observation of a copper rich ( $\alpha_2$ ) surface layer by these workers was a consequence of the alloying procedure which they used<sup>3</sup>. In general, both phases can coexist at the surface, and their relative proportion depends on the heat treatment. Hydrogen chemisorption on the alloys, however, provides a chemical potential acting to draw nickel preferentially towards the surface layer<sup>4</sup>. The cooling of a copper-nickel alloy, so heated in hydrogen, to less than about 300° C then favours the formation of an  $\alpha_1$  skin covering the crystallites. Departures from a uniform catalytic activity may be expected only at the extremes of composition, namely, at 98–100 per cent nickel and at nickel contents insufficient to form a surface of the  $\alpha_1$  phase.

The constancy of activity and course kinetics observed for hydrogenation of butene-1 are in accordance with this view. Other results<sup>5,6</sup> with copper-nickel alloys prepared by reduction from mixed salts show the appearance of nickel-rich "skins" on the metal crystallites which can probably now be ascribed to the effect of hydrogen-reduction. The evaporated alloy-film technique avoids the possibility of spatial fractionation of the metals inherent in co-precipitation and thermal decomposition stages in chemical preparation of alloys and permits a single explanation of surface enrichment in transport actuated by hydrogen.

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Received April 12, 1967.

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### Dimeric and Tetrameric Complexes of Copper(O)

STABLE compounds of copper(O) appear to be unknown except for the barium salt of the complex acetylide anion  $[\text{PhC}\equiv\text{C}-\text{Cu}-\text{C}\equiv\text{CPh}]^{2-}$  described by Nast *et al.*<sup>1</sup> and perhaps a phthalocyanine complex<sup>2</sup>. Derivatives of copper(O) if monomeric should be paramagnetic ( $4s^1$