JOURNAL OF CATALYSIS 6, 314-335 (1966)

# NOTES

## On the Surface Composition of Cu-Ni Alloy Catalysts

Recently Sachtler and co-workers (*1–3*) presented evidence that thin Cu-Ni alloy films separate into two phases at low temperatures (~200°C): a very nickel-rich kernel surrounded by a copper-rich alloy surface phase. (The miscibility gap stems from an endothermic heat of alloying.) It was further shown that the composition of these two phases was independent of the overall composition of the alloy throughout the two-phase region. Sachtler and Jongepier (*3*) went on to suggest that the available catalytic data (*4–9*) for granular Cu-Ni catalysts are generally consistent with the view that the alloy phases have equilibrated on the surface, if not in the bulk (*9, 10*). They then remarked:

> The composition of the surface of an equilibrated alloy should, in general, depend on the ambient atmosphere. Accordingly, for alloys reduced with hydrogen or films equilibrated in a hydrogen atmosphere, one might expect that the surface is enriched in nickel, as hydrogen is strongly chemisorbed on nickel, but only negligibly adsorbed on copper. This additional effect seems to be small, however. The films described in our previous article were prepared under ultrahigh vacuum whereas the films studied by Gharpurey and Emmett had been sintered in hydrogen and the granular catalyst used by Takeuchi *et al.*, Hall *et al.*, and Russell *et al.*, were prepared by a reduction with hydrogen. The absence of a drastic effect of hydrogen becomes less surprising, if one considers the small amount of chemisorption of that gas at the temperatures (300° or 350°) used by the authors mentioned.

It is the purpose of the present communication to point out that the well documented (*4, 8, 12–14*) promoting effect on the catalytic activity of Cu-Ni alloys, caused by cooling in hydrogen rather than in vacuum, could be explained by the assumption that the catalytic activity of the surface alloy phase is increased by enrichment with Ni (and that the activity of the "pure" Cu catalyst is enhanced by the concentration of minute amounts of active impurities, such as Ni, at the surface). This phenomenon has been found for the hydrogenation of ethylene, $H_2$–$D_2$ exchange and ortho–para $H_2$ conversion; all of the alloys, as well as Cu catalysts, were strongly promoted by treatment in $H_2$. Conceivably, the effect on catalyst activity might be a more sensitive test for Ni enrichment in the surface than other methods applied to date.

The activities of Cu-Ni alloys for reactions which occur at subzero temperatures can be changed from one stable state to another by cooling in $H_2$ from the reduction temperature (e.g., 250°) instead of evacuating above 100° before cooling. If enrichment of the surface phase with Ni by the chemisorption of $H_2$ is the correct interpretation, then the mobility of Ni must be quenched at lower temperatures, i.e., enrichment does not occur below ~100°.

An extraction of nickel from the alloy phase above 150° was reported by Scholtus and Hall (*15*) in their studies of the hysteresis in the $H_2$ isotherms from alloys prepared from precipitated powders. It was shown that during the initial reduction of the mixed oxides to form the alloys, $H_2O$ was encapsulated; this reacted with Ni of the alloy, on lowering the $H_2$ pressure, releasing $H_2$ and forming NiO. Assuming a homogeneous (or Cu-rich) alloy interface, the Ni atoms evidently were moved appreciable distances through the bulk phase via the potential supplied by chemisorbed oxygen.

A word of caution should be added. Although the two-phase Cu-Ni alloy system offers a reasonable and natural explanation for many observations, it leaves other questions unanswered. Thus, if the promoting effect of $H_2$ on the catalyst activity is due to increasing the Ni concentration in the surface, it is not clear why the enhancement is strongest near 80% Cu where only one (alloy) phase is expected (*4*b). Moreover, pure nickel catalysts and other pure transition metal catalysts were poisoned by the same treatment (12), indicating that a different explanation is required for these. Although the activity for hydrogenation of ethylene (*4*b), for $H_2$–$D_2$ exchange and p-$H_2$ conversion (*7*) and heat of adsorption of $H_2$ (*8*) qualitatively agree with Sachtler's picture, data for the hydrogenation of benzene (*4*a) do not. In the last and related cases, there is a distinct correlation with the filling of the *d* band. Moreover, quantitatively the activities for the remaining reactions do diminish continually in the two-phase region. Finally, it is not clear why evidence of bulk diffusion is found in some cases and not in others. Hall and Alexander (*10*) showed that alloying of small crystallites of Cu and Ni must occur after reduction of the mixed oxides. Although the nominal conditions of the reduction were overnight at 350°, higher temperatures were momentarily attained as a glowing zone passed through the bed in the initial stages of the reduction. However, Hall and Hassell (*12*) avoided this "glow phenomenon" by initiating the reduction in streams of $H_2$-He mixtures, yet X-ray patterns from these catalysts still indicated they were well alloyed as judged by lack of line twinning. Moreover, in neither case did the alloys segregate when annealed for many hours in flowing $H_2$ at 250° or 350°. Russell and co-workers (*7, 9*) found well-alloyed catalysts which had been reduced at 500° and annealed in $H_2$ at 350°. If Ni atoms can diffuse at 150° to precipitate NiO (*15*), if Cu atoms can diffuse to enrich the catalyst surface (*1–3*) and if Ni atoms are pulled into the surface by action of the ambient atmosphere, it seems surprising that some evidence of phase separation has not been reported. Further work, designed to understand these shortcomings, should add materially to our understanding of catalysis over metals.

## Acknowledgment

This work was sponsored by the Gulf Research & Development Company as part of the research program of the Multiple Fellowship on Petroleum.

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*Received April 4, 1966;*
*revised May 27, 1966*