The Surface Composition of Reduced-Oxide Copper–Nickel Alloys

Numerous studies of metal alloy surfaces have been carried out in order to establish the role of the collective "electronic factor" in metal catalysis or alternatively the degree to which a surface atom may retain its individuality. Particular attention has been paid to the copper–nickel alloy series in this regard (*1–8*) since this system apparently has the capability of forming a series of alloys of continuously changing bulk composition. Understanding of the wide variety of results obtained has been greatly assisted by the predictions (*9*) and work (*6*) of Sachtler *et al.*, who pointed out that when such alloys were annealed within a specified temperature range a phase separation could take place resulting in a fixed copper-rich surface composition over a wide overall compositional range.

In one recent investigation (*8*), however, the authors suggest that provided a "proper" preparative procedure is carried out surface and bulk compositions alike will have an identical (overall) composition. The preparative procedure followed in their case consisted of melting and mixing purified materials followed by a "not too slow" quenching. LEED studies were limited to one crystal face (110) and the identical nature of the surface and bulk was established using Auger spectroscopy. While a more extensive LEED survey might have been desirable, and while surface preparation for Auger studies have been shown to significantly affect the surface composition (*10*), it would seem that the predicted Sachtler phase separation can be avoided.

The point to which we would like to address ourselves concerns the reason for the observed phase separation in copper–nickel alloy thin films: their high defect structure. We feel that it is important to show that the situation pertaining to thin films should not be regarded as an exceptional case and in particular that more practical catalytic materials such as powder or granular catalysts (supported or unsupported) may also undergo such a phase separation.

In a previous publication (*5*) we attempted to achieve this objective using low-temperature hydrogen adsorption or titration to investigate the surface composition and powder X-ray diffraction to establish that of the bulk for a series of copper–nickel alloys. Regrettably, while the results did indicate differing surface and bulk alloy compositions roughly in accord with Sachtler's prediction, they were open to several objections:

(a) The amount of hydrogen adsorbed by the nickel sample appeared to be unusually high.
(b) Hydrogen adsorption on the alloys while of the correct relative order of magnitude, showed considerable scatter.
(c) Hydrogen adsorption was observed on the (slightly impure) copper sample.

On subjecting the copper and nickel samples to purification and high-temperature sintering treatment, objections (a) and (c) above were effectively removed (*11*), leaving only the somewhat random scatter in the maximum amount of hydrogen adsorbed on the alloys to be dealt with.

Four copper–nickel alloys were selected of composition 10.35 ± 0.02, 28.83 ± 0.09, 47.71 ± 0.05, and 77.15 ± 0.04 atom % copper as determined by electrodeposition techniques. The samples were prepared from the appropriate mixture of nitrates from which the mixed basic carbonate and oxide were formed, the final sample being obtained by reduction in a stream of hydrogen (*5*, *12*). In order to produce a two-phase alloy system we attempted to maximize the production of defects to enhance surface diffusion and phase separation. This was done by reducing the oxides at the minimum possible temperature [approximately 137°C for the 10.35 and 100°C for the 77.15 atom % Cu sample, respectively (*5*)] prior to raising the temperature to 350°C for 12 hr for the final reduction. [Preparative technique no. 1 of Ref. (*11*).] Bearing in mind problems associated with ambient gases controlling the surface composition the system was then evacuated to 10^{-6} Torr at 350°C and thus maintained for approximately 192 hr. This was followed by a lengthy (48 hr) period of cooling to room temperature. In this way we hoped to give ample opportunity for surface diffusion and phase separation to occur and to remove excessive surface defects (*13*).

All samples were prepared *in situ* in a gravimetric (Cahn R. G.) microbalance used for adsorption studies (*5*). Hydrogen adsorption and surface area measurements (N_2) were carried out at −196°C. Special problems associated with the use of a microbalance under such circumstances were minimized and allowed for in the microbalance calibration (*14*). The hydrogen isotherms were type I, BET classification (*15*) with a maximum amount being adsorbed at approximately 2×10^{-3} Torr. For the sake of brevity only the maximum amounts are given here. Figure 1 illustrates these amounts ($\mu g/m^2$) as a function of overall composition (atom % Cu). The solid line illustrates the behavior to be expected were the Sachtler phase transition (*9*) to take place, adjusted to allow for our differing maximum temperature. The broken line predicts the behavior were the surface to remain a continuous series of solid solutions. In either case the assumption is made that the contribution of each atom in the surface is that which it would make in the pure metal: i.e., each nickel atom would adsorb one hydrogen atom (*13*, *16*) while copper would adsorb none (*17*). The data for copper and nickel were previously reported (*11*). All points are ±0.3 μg. X-Ray powder diffraction techniques indicated that the bulk and overall compositions were virtually identical: i.e., that of a series of solid solutions obeying Vegard's rule (*12*).

The results as illustrated in Fig. 1 clearly illustrate that a phase separation, roughly in accord with the predictions of Sachtler, has taken place and that the copper-rich surface composition is constant over a wide bulk compositional range. The small difference from the Sachtler prediction (~2 μg

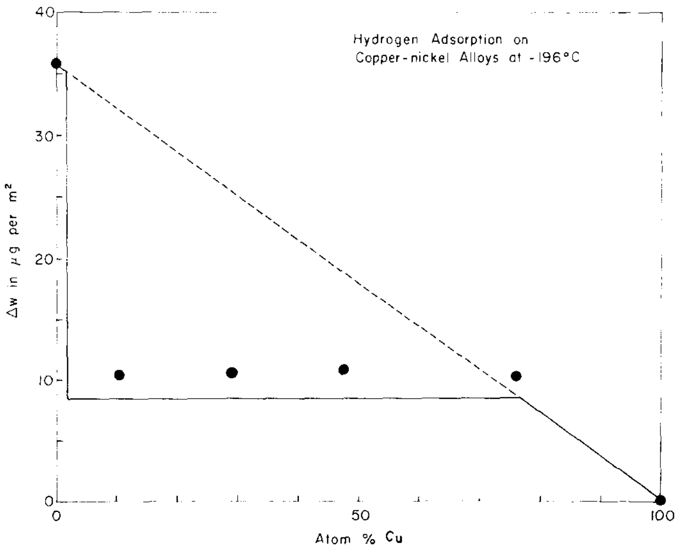

FIG. 1. Hydrogen adsorption on copper-nickel alloys at −196°C. For a detailed explanation see text.

in each case) could be explained by suggesting that the surface has a slightly higher nickel content than predicted, or that the surface atoms do not behave precisely as they do in the pure metals, or both. Since the two sources of the prediction (*18*, *19*), are in good agreement on the surface composition for an approximate annealing temperature of 350°C and since there is increasing evidence that atomic surface electronic properties are modified by the atoms' immediate environment (*8*, *20*, *21*), we prefer the latter explanation.

Clearly, the phenomenon of phase separation on the copper–nickel system (and presumably other similar systems) is not confined to thin metal films but may also occur in powdered or granular materials. In the latter case, however, phase separation is limited to the surface phase. Presumably if the deposited films were greatly in excess of (say) 100 Å, here also phase separation would be incomplete. Since in the case of Ertl and Küppers (*8*) an attempt seems to have been made to avoid phase separation and since in our case an attempt was made to achieve it, we would deduce that most preparations would result in some type of intermediate situation. Finally we believe our data indicates clearly the reasonable assumptions that the behavior of an individual surface atom, when surrounded by atoms of a similar but not identical metal, will be modified, and that this must be taken into account when carrying out a surface titration. Regrettably at this time we are not able to quantitatively predict the extent of this modification.

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