Electronic Ligand Effects in Nickel Alloy Catalysts

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Summary Data are presented to show that the effect of alloying an inactive metal with a catalytically active metal is electronic rather than geometric in origin.

Two categories of reaction over heterogeneous catalysts have been identified.[1] Reactions such as hydrogenation are facile, whereas hydrogenolysis and self-poisoning reactions are demanding. The former reactions can occur on isolated metal atoms; the latter reactions require larger numbers of contiguous metal atoms.[2] There is disagreement concerning the number of metal atoms (n) which constitute the active site for demanding reactions. Data for Pt metal catalysts indicate that only 1 or 2 adjacent sites are required,[3] whereas recent data for Ni–Cu alloys[4] seem to show that $n = 12$ for ethane hydrogenolysis, 17 for propane, and 20 for butane hydrogenolysis. The evidence for large values of n is that the decrease in the activity of Ni–Cu alloys (Cu itself is inactive) is paralleled by a decrease in the pre-exponential term whereas the activation energy remains unchanged. On the other hand, data for Ni–Pd alloys[5] (Pd like Cu is essentially inactive) show that there is only a small loss of activity when Ni is diluted with Pd. Figure 1 compares the activity of Ni–Cu and Ni–Pd alloys for the hydrogenolysis of ethane. If a geometric effect operates in Ni–Cu alloys one questions why a similar effect is not found in Ni–Pd alloys.

It is difficult to envisage a molecular process in which, for example, a butane molecule as it adsorbs on a metal surface disintegrates completely in a single step into 4 C atoms and 10 H atoms. The *simultaneous* cracking of 3 C–C and 10 C–H bonds seems improbable. A stepwise dissociation would appear more likely, but this would not require the simultaneous availability of 20 Ni atoms since H atoms once abstracted from the butane can migrate away from the active site thus freeing the Ni atom for further H abstraction. The apparent discrepancy between the statistically calculated number of sites ($n = 20$) and the expected number of sites assuming a stepwise dissociation ($n = 2$ Ni per C atom) can be removed if account is taken of the electronic influence of the nearest-neighbour atoms in a metal alloy.

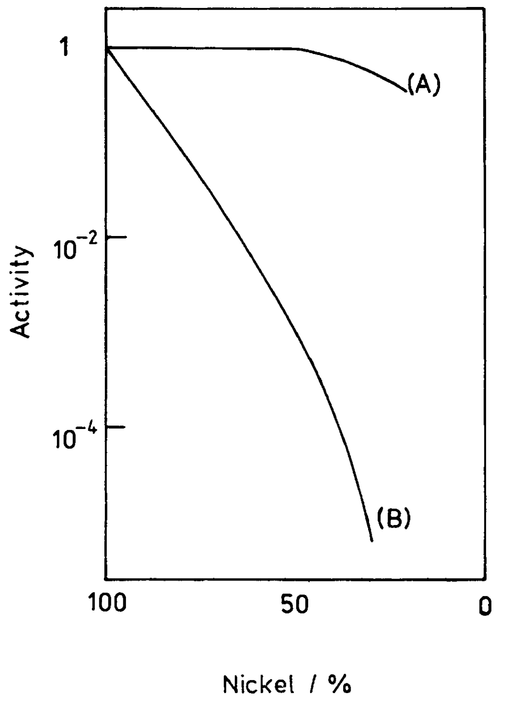

FIGURE 1. Relative specific activity of Ni–Cu (after ref. 4) and Ni–Pd alloys (after ref. 5) for the hydrogenolysis of ethane: (A), Ni–Pd; (B), Ni–Cu.

The photoelectron spectra of Ni–Cu alloys[6] show that the band structures of the binary alloys are similar to weighted averages of the band structures of the parent elements. This has led to the conclusion that Cu atoms have little influence electronically on their Ni neighbours.[2]

This is not correct. Figure 2 shows schematically how the local density of states at a Ni atom is affected by its immediate environment. The important point is that although the *position* of the Ni 3d-band is hardly affected by adding Cu the band *width* is affected,[7] with the result that the d-band slips below the Fermi level, *i.e.* the d-band becomes filled. The band width is proportional to the number of near neighbour atoms which are 'like' atoms,[8] *i.e.* Ni atoms in this case. As the Cu content of a bulk alloy is increased there is a progressive narrowing of the d-band of the Ni, with the result that the local density of states at a Ni atom decreases as its near-neighbour Ni atoms are substituted by Cu atoms. The overall effect is to cause the Ni atom to become less Ni-like. Since it is necessary to form strong metal–carbon bonds for hydrogenolysis to occur, a decrease in the local density of states, coupled with a filling of the Ni 3d-band, will result in weaker Ni–C bonds and a decrease in hydrogenolysis activity.

We suggest that the calculated value of $n = 12$ for ethane hydrogenolysis[4] arises not because 12 Ni atoms are directly bonded to the ethane, but rather because this is the minimum size of Ni cluster which ensures that the *central* Ni atoms have only Ni atom near neighbours and, therefore have true Ni-type d-orbitals. A simple calculation for a Ni(100) plane shows that if initially each C atom forms single bonds to two Ni atoms (requiring 4 Ni atoms in all) the size of cluster required to ensure that the central 4 Ni atoms have only Ni atoms as near neighbours is 12, *i.e.* the same value as obtained from the geometric model.

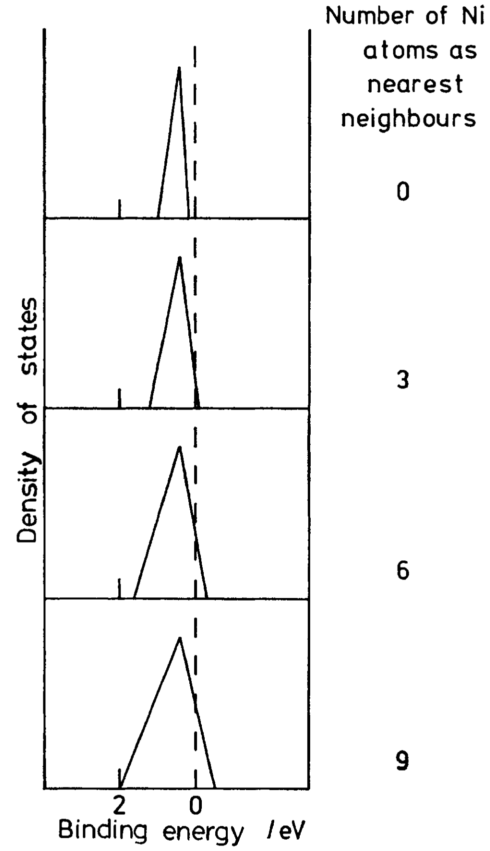

FIGURE 2. Variation in the local electron density of states at Ni atoms as a function of the number of near neighbour atoms which are Ni atoms (after refs. 6 and 7).

The present model accounts also for the difference between Ni–Cu and Ni–Pd alloys (see Figure 1). In the case of Ni–Pd alloys both metals have unfilled d-bands so there is a greater probability of forming a combined d-band and so unfilled d-orbitals will be found at Ni atoms even at high Pd contents.

The model is not restricted to Ni alloys. There is growing evidence of electronic ligand effects in many other alloy catalysts.[9] Similar electronic effects due to adsorbed sulphur-containing molecules may account for the lower hydrogenolysis activity of partially sulphided catalysts.

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