

Ligand Effects in Catalysis by Alloys

Recently Palazov *et al.* (1) published a very interesting paper dealing with the relative importance of the so-called "ligand effect" and "ensemble size effect" in catalysis by alloys. However, some conclusions of their paper are debatable.

Palazov *et al.* (1) state in their discussion that inhibition of the "facile" reaction of cyclohexane to benzene can only be explained by a ligand effect. However, there are indications that the hydrogenation of benzene, or its reverse the dehydrogenation of cyclohexane, are sensitive to the geometry of the surface. The reactions seem to behave in a "facile" manner on Ni-Cu alloys (i.e., they are insensitive to alloying) but not on Pt-Au (2). An explanation could be that Ni-Cu alloys contain bigger Ni clusters than the Pt clusters in Pt-Au. Furthermore, there are several homogeneous mononuclear systems catalyzing the hydrogenation of olefins, but there is no reliable evidence for the hydrogenation of benzene by comparable systems. This rather suggests that the dehydrogenation of cyclohexane (which is not equal to an aromatization step by dehydrogenation) could be a "demanding" reaction, i.e., sensitive to alloying.

A second point is that Palazov *et al.* (1) suggest that the frequency decrease of the ir absorption band of CO on Pt upon coadsorption with ethylene or upon alloying Pt with Pb both indicate an electron shift toward Pt. However, a "combination" of alloying Pt by Pb and coadsorption with ethylene does not lead to an extra decrease of the frequency (Ref. (1), page 6). This seems illogical: why should there exist such a sudden and severe limit to the ability of Pt to accept electrons?

However, in both cases another effect is also operating: ethylene as well as Pb dilute the layer of the interacting CO dipoles on Pt and this dilution leads also to a decrease of $\nu(\text{CO}/\text{Pt})$. The question of the relative importance of these effects, electronic vs geometric ones, is therefore important.

A separation of the two effects can be obtained by performing experiments with various ratios $^{12}\text{CO}/^{13}\text{CO}$. Extrapolating the values for $\nu(^{12}\text{CO}/\text{Pt})$ to infinite dilution by ^{13}CO , we obtain the frequency value without dipole-dipole coupling since only equally vibrating dipoles interact strongly (see, e.g., Refs. (3, 4) for more details). We have performed these experiments and the results may be of interest to the authors and readers of Ref. (1).

Experiments with a Pt-Cu alloy (5) have shown that the effect of Cu on $\nu(\text{CO}/\text{Pt})$ which amounts about 40 cm^{-1} can be ascribed to a dilution effect. When CO is coadsorbed with ethylene, the major part (over 60%) of the total effect is again dilution (4). Only a smaller residual part of the total effect might be ascribed to a ligand effect of ethylene, although it cannot be completely excluded that a corrosive (roughening) effect of ethylene adsorption (6) may also be involved. Nevertheless, the major effect in both cases is a geometric effect (dilution) and it is not surprising therefore that there exists a natural limit to the negative frequency shifts, viz., the infinite dilution. Because of the nature of the effect (dipole-dipole interaction) we may conclude that any alloying of Pt will probably produce a geometric (dilution) effect on $\nu(\text{CO}/\text{Pt})$ of about 40 cm^{-1} . Our results on ir spectra with Pt-Pb alloys confirm this picture: a large part of the effect of Pb on

$\nu(\text{CO}/\text{Pt})(>50\%)$ is again geometric, but a part of the total effect is not geometric and might be ascribed to a ligand effect (7). However, Palazov *et al.* (1) only mention the possibility of increased dispersion of Pt due to the addition of Pb. They completely neglect even the possibility of a dilution effect of Pb on the frequency of CO adsorbed on Pt, although they do mention it as a possible factor in the catalytic experiments. Summarizing, the expected ligand effect is either below the detection limits (as with Pt/Cu and probably with all other alloy systems which are less exothermic) or at least considerably smaller than appearing at first glance from the observed shifts with pure $^{12}\text{C}^{18}\text{O}$. The question now is how essential this ligand effect might be in those cases where it can be proven experimentally.

Let us compare the results with three alloy systems:

(1) Ni–Cu. The number of Ni *d*-electrons remains constant (8), the size of the $\nu(\text{CO}/\text{Ni})$ shifts [50 cm^{-1}] (9) can probably be explained by a dilution effect, and destructive reactions are strongly suppressed by alloying (10).

(2) Pd–Ag or Pd–Au. The number of Pd *d*-electrons varies upon alloying (11), the size of the $\nu(\text{CO}/\text{Pd})$ shift can probably be explained by a dilution effect [30 cm^{-1}] (12) and destructive reactions are again strongly suppressed by alloying (13).

(3) Pt–Pd. The size of the $\nu(\text{CO}/\text{Pt})$ shift is larger than a pure dilution effect (1, 7), and destructive reactions are strongly suppressed (1).

The conclusion is obvious, the suppression of the destructive reactions observed with the above mentioned systems is linked with the dilution effect which is the com-

mon feature to all three. Destructive reactions are evidently suppressed by the elimination of the big ensembles required for these reactions and not by the postulated ligand effects which are possibly present in the Pt–Pb case.

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