A Possible Indication of Ligand Effects in Alloying

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A part of the large frequency shift for CO adsorbed on a strongly exothermic alloy like Pt–Pb may possibly be ascribed to a ligand effect.

The changes in the catalytic behaviour of metals caused by alloying are usually thought to originate from the geometric or ensemble size effect and the electronic or ligand effect.[1] The former includes all phenomena related to the change in the average size of the ensembles of active atoms or in their composition (mixed ensembles).[2] This is the main effect when the perturbation by alloying is weak.[3] The second effect includes all phenomena related to changes in the electronic structure of the alloy components (*e.g.* refs. 4 and 5). Often the effects of alloying are considered to be too large to be explained by a geometric effect alone,[5] *e.g.* an overall decrease in the heat of adsorption[6] or the so called synergistic effect[5] (a higher activity for the alloy than for the sum of the pure components). However, a change, by alloying, in the adsorption site[9] or a suppression of self-poisoning side reactions may very well explain these phenomena.

The most reliable piece of evidence, so far, in favour of a ligand effect seems to be the ν(CO) shift, *i.e.* the shift, upon alloying, of the frequency of the i.r. absorption band of CO adsorbed on a Group 8 metal.[7,8] However, as explained in our previous paper,[10] this ν(CO) shift is not free from geometrical aspects. The electrodynamic interaction between the equally vibrating CO molecules (dipole–dipole coupling) is strong and causes an increase in the frequency with increasing surface coverage θ(CO). As explained before,[10] this effect can be eliminated by using the results of the adsorption of several isotopic mixtures of ^{12}CO–^{13}CO. There is no coupling between CO molecules with a different absorption band frequency as for ^{12}CO and ^{13}CO. Upon plotting the frequency data against the adlayer composition, the frequency without dipole–dipole coupling is obtained by extrapolating these data to infinite dilution of ^{12}CO by ^{13}CO. If the observed effect (*e.g.* of alloying) on ν(CO) were purely 'geometric', the extrapolated frequencies for alloy and pure metal should be equal, as found with Pt–Cu.[11] However, if a part of the total effect were 'electronic', a proportional difference in the extrapolated frequencies should be observable.

Alloys which are formed less exothermically than Pt–Cu, like Pd–Ag, Pd–Au, Ni–Cu, and Pt–Au are not expected to reveal any important electron shift. However, the situation

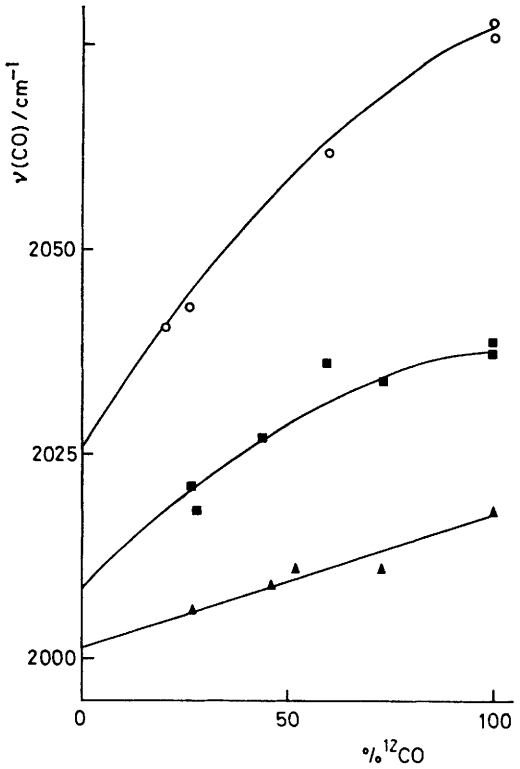

Figure 1. Frequency of the i.r. absorption band of CO adsorbed on Pt as a function of the isotopic composition of the CO layer. ○: Pt on alumina. ■ : Pt–Pb (88:12) on alumina. ▲: Pt–Pb (41:59) on alumina.

may be different with alloys which are formed more exothermically than Pt–Cu; alloys like Pd–Zr[12] or Ni–Al[13] do show relevant shifts in the electron energy.

The Pt–Pb system seemed a suitable choice to verify this idea. While a Pt–Cu(50:50) alloy has an enthalpy of formation of about −10 kJ/mol,[14] the value for a Pt–Pb (50:50) alloy is −27 kJ/mol.[15] Also from a catalytic point of view there was a reason for this choice. A recent study by Palazov *et al.*[16] ascribes the effect of Pb on Pt, which improves the catalytic behaviour of Pt, primarily to an electronic ligand effect. Therefore, more quantitative data on the size of a possible electronic effect seemed desirable.

Two Pt–Pb alloys were prepared by homogeneous precipitation using the hydrolysis of urea.[17] Experimental details of catalyst preparation and i.r. technique have been described elsewhere.[8,10] As determined by *X*-ray fluorescence spectroscopy the alloys contained 88 and 41% of Pt respectively. The results concerning the frequencies of the high-frequency bands are shown in Figure 1.

As can be seen immediately, the situation is different from that encountered with Pt–Cu.[11] The extrapolated frequencies do not coincide as they did with Pt–Cu. From the total effect of 55 cm^{-1} [in the case of the Pt–Pb (41:59) alloy] about 30 cm^{-1} should be ascribed to a geometric effect of dilution. A maximum of 25 cm^{-1} (*i.e.* 45% of the total effect) is then the margin within which a ligand effect may operate. It should be noted, however, that our result is not yet definite evidence of an electronic effect of this size.

The consequences of this possible ligand effect on the catalytic behaviour of Pt can only be determined by a detailed comparison of the results obtained from Pt–Pb alloys with those obtained under identical conditions from alloys like Pt–Au or Pt–Cu, which will reveal only the ensemble size or geometric effect of alloying.

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