

Geometric and Ligand Effects in the I.R. Spectra of Carbon Monoxide adsorbed on a Platinum–Copper Alloy

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Summary The origin of the frequency shift for CO adsorbed on alloys has been established and does not involve a ligand effect.

ALLOYING can change the activity and selectivity of individual metals in catalytic reactions. During the last

decade it became clear that alloying of an 'active' metal with an 'inactive' one suppressed those reactions which required large ensembles of active atoms. This is called a 'geometric' or 'ensemble size' effect.^{1,2} On the other hand, it has often been pointed out that the components of an alloy are also changed electronically. For example, a mutual transfer or

shift of electrons could alter the chemisorptive properties of the individual components of an alloy. This is usually called an 'electronic' or 'ligand' effect.^{1,2}

The results of i.r. spectroscopic investigations of the CO adsorption on alloys of a Group 8 metal with a 1b metal have often been presented as evidence for such a ligand effect. Experimentally it has been found that (i) the frequency of the i.r. absorption band of carbon monoxide adsorbed on the Group 8 metal decreases upon dilution with the 1b metal,³⁻⁵ and (ii) the frequency of the i.r. absorption band of CO adsorbed on the 1b metal increases upon dilution with the Group 8 metal.^{4,5} These facts were explained by an assumed electron shift from the 1b metal to the Group 8 metal.^{4,6} As a result, the extent of backdonation into the antibonding orbitals of CO adsorbed on the Group 8 metal would increase, thus decreasing the frequency, while the opposite would occur on the 1b metal. In a previous paper,⁵ we explained comparable results on a series of Pt-Cu alloys by assuming an increased 'individualisation' of the metal atoms by alloying. We assumed that this would lead to an increase in the extent of direct- and back-donation in the CO bonding. The relative importance of these effects would then cause a net increase or decrease in the absorption band frequency.

However, up till now no one has acknowledged sufficiently the following effect. It is well known that equally vibrating dipoles like ¹²CO molecules adsorbed on a metal experience electric coupling, thereby increasing their stretching frequency.⁷ Since the dipoles formed by the CO molecules adsorbed on, say, Pt and Cu clearly have a different stretching frequency, their electric coupling is negligible. Coupling, therefore, occurs only between CO molecules adsorbed on the same metal. A full coverage of CO adsorbed on an alloy is therefore comparable with a lower surface coverage on a pure metal. We mentioned this effect in our previous paper⁵ but were not able to establish exactly the size of the dipole-dipole coupling effect in the adsorption of CO on supported metals and alloys.

The dipole-dipole coupling between adsorbed CO molecules can be eliminated by the so-called 'isotopic dilution method' introduced theoretically by Hammaker *et al.*⁷ With this method the ¹²CO molecules in a CO adlayer are successively replaced by ¹³CO molecules. Since ¹²CO and ¹³CO vibrate with a different frequency ($\Delta\nu = ca. 50 \text{ cm}^{-1}$) their coupling will also be negligible. By extrapolating the values of the high-frequency peaks (characteristic of the ¹²CO vibrations) of several mixtures to infinite dilution by ¹³CO, one obtains the frequency value free of the dipole-dipole coupling effect. In this way, it is possible to estimate the extent of the electronic and/or diluting effect of, say Cu on the absorption band frequency of CO adsorbed on Pt. If the effect of Cu is purely electronic ('ligand' effect), then it should be the same for a pure ¹²CO layer as for a layer diluted with ¹³CO. However, if the

effect is purely geometric (by dilution of the layer) then further dilution by ¹³CO should have only a reduced effect. For other details of the isotopic dilution method, see ref. 9.

We have performed experiments with two samples: one with pure Pt and one with Pt containing 50% Cu. Preliminary results by Auger electron spectroscopy⁸ indicate a surface concentration of about 35% Pt. Both metal and alloy were finely dispersed on alumina (Aluminium Oxid C—Degussa) and had a particle size of about 20 Å as estimated by electron microscopy. The isotopic mixtures were prepared by consecutive administration of ¹²CO and ¹³CO into a vessel equipped with a calibrated Pirani gauge. Further experimental details have been described elsewhere.⁵

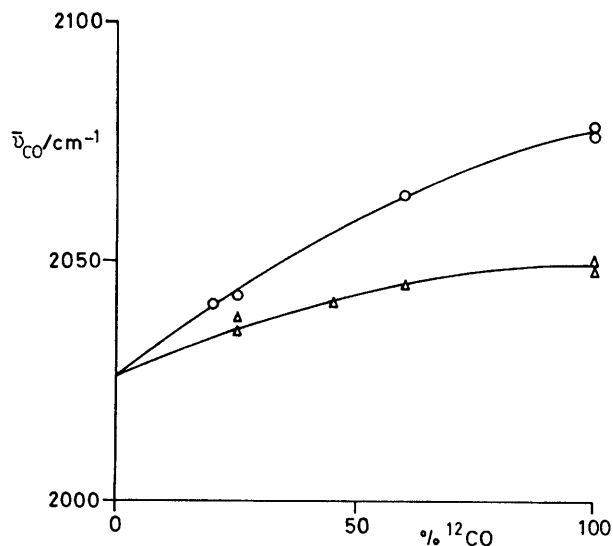


FIGURE. Frequency of the i.r. absorption band of CO adsorbed on Pt as a function of the isotopic composition of the CO layer. ○: Pt on alumina, △: Pt-Cu 50/50 on alumina.

The results are collected in the Figure. The frequency values are obtained after adsorption of sufficient CO to maximize the absorption band of CO on Pt while the band of CO on Cu is still just not visible. From the Figure it is immediately clear that both curves converge to practically the same value upon increasing dilution by ¹³CO. In other words, the frequency decreasing effect of Cu on the absorption band frequency of CO adsorbed on Pt can be explained by a decreased dipole-dipole coupling. An electronic effect, if operating at all, is, at least with the Pt-Cu system, below the detection limit of the method used in this paper. Alloys of other compositions fully confirmed the result and conclusion presented here.

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