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On Electronic and Geometric Effects of Alloying

An Infrared Spectroscopic Investigation of the Adsorption of Carbon Monoxide on Platinum–Copper Alloys

F. J. C. M. TOOLENAAR, F. STOOP, AND V. PONEC[1]

Gorlaeus Laboratoria, Rijksuniversiteit Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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The adsorption of CO on alumina-supported Pt–Cu alloys was studied. The results were compared with those obtained on the unalloyed Al_2O_3-supported metals as well as with the results on alloys supported on silica. By use of the isotopic dilution method it has been established that the downward shift of the frequency of the CO/Pt band observed upon alloying Pt with Cu is "geometrical," caused by dilution of Pt by Cu; an electronic or ligand effect was not observed (within the limits of error). The upward shift of the frequency of the CO/Cu band upon alloying Cu by Pt is most probably caused by "individualization" of the Cu atoms in the Pt layer.

INTRODUCTION

Alloying of metals may result in important changes in their activity and selectivity in catalytic reactions (*1*). These changes are experimentally well established, but theoretically still not fully understood. The main problem is the question of the relative importance of the various factors which may be responsible for the variations. There is currently a very lively and continuing discussion on this important matter (*2*–*4*).

When a metal which is active in a certain reaction is alloyed with an inactive one, two effects can be conceived (*2, 5*):

(1) A "geometric" or "ensemble size" effect. By alloying, the number of contiguous identical atoms is clearly decreased. Catalytic reactions which require large ensembles of active atoms will then obviously be suppressed more strongly than reactions which require only small ensembles.

(2) An "electronic" or "ligand" effect. The electronic structure of the metals may be changed by alloying. If so, then the bond strength of the adsorbed species and thereby their reactivity may change as well.

As far as the latter effect is concerned, it is important to establish which changes are experimentally and theoretically well documented and which are only apparent. Contrary to the assumptions made in the early literature (see Ref. (*6*) for a review) a real transfer of electrons between the components of an alloy is the exception rather than the rule (*7*). For convenience, two groups of alloys may be discerned:

(i) Very strongly exothermic alloys, such as Ni–Al, Ni–Ga, Pd–Zr, Pt–Zr. Bonding in these alloys reveals features which recall covalent (localized) bonds. These alloys prefer to exist in certain stoichiometric ratios, they are spatially ordered, etc. They are sometimes brittle and may even lose their metallic character, becoming semiconductors. Their formation is frequently accompanied by a downward shift in the energy of the valence bonds of both components (*8*).

(ii) Weakly exothermic or even endothermic alloys, such as Ni–Cu, Pt–Au, Pd–Ag, Pd–Au, Pt–Cu. The bonding in these alloys is much weaker and the individual components preserve their identity to a large extent. XPS studies reveal that the position of the valence bands is hardly changed by alloying (*9*) and this applies also to the spatial

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[1] To whom all correspondence should be addressed.

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distribution of the *d*-electrons (*10*). However, the width of the *d*-bands is reduced (*9*), which indicates that the overlap between the atoms in the alloy is smaller than in the pure metals. The individual components of the alloy may therefore change their behavior in the direction of free atoms.

Although these facts have been known and acknowledged already for some time (*11*), the exact consequences of the abovementioned changes due to alloying are still a matter of discussion. In particular, the importance of an "electronic effect" has been subject of many speculations.

It has been found experimentally that some alloys are catalytically more active than the individual alloy components. This could have the explanation that alloying might suppress competitive reactions or prevent the deposition on the surface of nonreactive species (e.g., carbonaceous residues in hydrocarbon reactions) due to the different requirements of the just mentioned reactions with regard to the size of the active ensembles. However, in such cases and also when weakly exothermic or even endothermic alloys were involved, most authors preferred to speculate on synergism, i.e., a mutual activity enhancement, by an assumed ligand effect of alloying (*12*). The ir spectra of CO adsorbed on these alloys are often presented as the most important if not the sole evidence for this synergistic effect, with the frequency shifts observed upon alloying being ascribed to a ligand effect. It is therefore important to establish the contribution of the ligand effect to these shifts.

The basic idea behind the ligand effect of alloying is as follows. When CO is adsorbed on a Pt atom surrounded by Cu atoms (with more outer shell *spd*-electrons than Pt), the *d*-electrons of this Pt atom are more easily back-donated into the antibonding 2π-orbitals of CO than when the same atom is surrounded by other Pt atoms. As a result, the CO bond is further weakened and the frequency of the ir absorption band of CO is lowered on alloys. However, it is a well known fact that this frequency is also very sensitive to the mutual distance of the CO molecules adsorbed on the surface. Dipole–dipole (*13–16*) or vibrational (*17*) coupling can be responsible for an upward shift of at least 30 cm^{-1} with respect to the singleton frequency. It is obvious that by alloying Pt with Cu, one also increases the average mutual distance between the CO molecules adsorbed on Pt, thereby reducing the CO–CO dipole coupling. We wish to establish the size of the dilution effect in order to evaluate the margin remaining for an additional electronic effect. This can indeed be done by using the so-called isotopic dilution method based on the ideas of Hammaker *et al.* (*13*) and recently successfully applied by several authors (*15–18*). In particular the papers by Crossley and King (*14–16*) formed the source of inspiration for this paper.

With the isotopic dilution method the ir spectra of several isotopic mixtures of adsorbed ^{12}CO and ^{13}CO are compared at "full" surface coverage. Below we will confine ourselves to only a short description of the principles of this method; for a more theoretical analysis, see Refs. (*13, 15, 17, 19–21*).

The isotopic dilution method is based on the following fact. Dipole–dipole coupling[2] is largest between dipoles with an equal singleton frequency, i.e., the frequency of the isolated molecules without any coupling. The coupling decreases upon increasing difference between the singleton frequencies; a difference of 30 cm^{-1} suffices already to make the coupling effect negligible. This means that dipole–dipole coupling between, for example, adsorbed ^{12}CO and ^{13}CO or between ^{12}CO/Pt and ^{12}CO/Cu can

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[2] The term dipole–dipole coupling, i.e., an electrodynamic "through-the-space" coupling, is used throughout for the sake of simplicity. However, vibrational coupling, i.e., coupling "through-the-metal" (*17, 20*), could cause the same effects. Moreover, a simultaneous operation of both mechanisms is also possible.

be neglected. On changing at θ(CO/Pt) → 1 from pure ^{12}CO to mixtures of ^{12}CO increasingly diluted by ^{13}CO, one gradually eliminates the dipole–dipole coupling. At "infinite dilution" ($x = {}^{12}\text{CO}/({}^{12}\text{CO} + {}^{13}\text{CO}) \rightarrow 0$) the frequency of an "isolated" molecule, the singleton frequency, is obtained. Now, if the effect of Cu on the absorption band frequency of CO/Pt were purely *electronic*, i.e., if it only changed the electronic structure of Pt and thereby the bond strength of C–O adsorbed on Pt, this effect should be the same regardless of the isotopic composition of the whole layer; two parallel curves $\nu = f(x)$ should result then (cf. Fig. 1a of Ref. (*22*)). However, if the effect were purely *geometric*, i.e., if it only increased the mutual distance between the CO/Pt molecules, Cu would essentially have the same effect as ^{13}CO; this effect would become smaller upon decreasing dipole–dipole coupling, i.e., upon increasing dilution by ^{13}CO, and disappear at "zero coupling"; as a consequence—at infinite dilution the two curves should coincide (cf. Fig. 1b, Ref. (*22*)). If both effects are operating an intermediate case should be expected; the remaining $\Delta\nu$ shift at infinite dilution would give then the maximum margin left for a ligand effect in the (CO/Pt)-frequency shift.

EXPERIMENTAL

All samples with alumina as carrier which are described in this paper were prepared by homogeneous precipitation with urea (*23*). Alumina was supplied by Degussa AG Frankfurt (Aluminum Oxide C, BET area 100 ± 15 m^2/g). Platinum (specpure, Drijfhout, The Netherlands) was dissolved in as little aqua regia as possible. Copper was used in the form of $Cu(NO_3)_2 \cdot 3H_2O$ (Baker, The Netherlands).

The bulk composition of the alloys was determined by X-ray fluorescence. The average particle size was below the detection limit of the X-ray diffraction measurements. Therefore, the formation of single-phase alloys could not be established with this method. Electron micrographs of all samples showed particles of 20 Å diameter or less.

The *in situ* treatment of the powders and the method adopted for the ir experiments were described elsewhere (*22, 24*).

Some results obtained with the alloys on alumina were compared with those obtained with alloys on SiO_2. The alloys on SiO_2 were of a considerably larger particle size and their phase compositions were checked by X-ray diffraction. Our earlier paper (*24*) should be consulted for more information concerning those alloys.

RESULTS

As already reported (*24*), alloying clearly affects the position of the ir absorption band maxima of adsorbed CO. The frequency of the CO/Pt band is gradually decreased upon alloying Pt with Cu while the CO/Cu band frequency is increased upon alloying Cu with Pt.

The alloys described previously (*24*) were all supported on SiO_2 and had an average particle size between 60 and 150 Å. Probably as a consequence of this relatively low dispersion, the ir absorption bands of adsorbed CO were too weak to allow isotopic dilution experiments of sufficient accuracy. However, it appears that on Al_2O_3 a much smaller particle size of the alloys can easily be obtained. We investigated three Pt/Cu alloys on Al_2O_3 with a 77, 42, and 31 bulk percentage of Pt and compared the results with those obtained with the alloys on SiO_2 as well as with the unalloyed metals.

The characteristic changes in the ir spectra of adsorbed CO caused by alloying Pt with Cu as well as the effect of isotopic dilution are shown in Fig. 1. Upon increasing the surface coverage, the frequency of CO adsorbed on unalloyed Pt increases due to the increasing dipole–dipole coupling until saturation has been achieved. The performance of this effect is somewhat complicated by the formation of islands of CO already at low surface coverage (*16*). (This

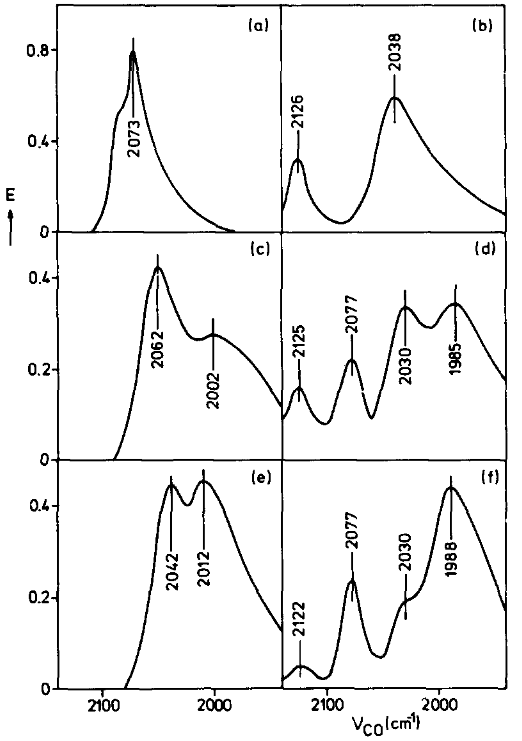

FIG. 1. Spectra of CO adsorbed on alumina supported Pt and Pt–Cu 31–69; total P_{CO} = 1.0 Torr. (a) Pt, ^{12}CO; (b) Pt–Cu 31–69, ^{12}CO; (c) Pt, ^{12}CO : ^{13}CO 60 : 40; (d) Pt–Cu 31–69, ^{12}CO : ^{13}CO 60 : 40; (e) Pt, ^{12}CO : ^{13}CO 25 : 75; (f) Pt–Cu 31–69, ^{12}CO : ^{13}CO 25 : 75. The wavenumbers of the band maxima are indicated.

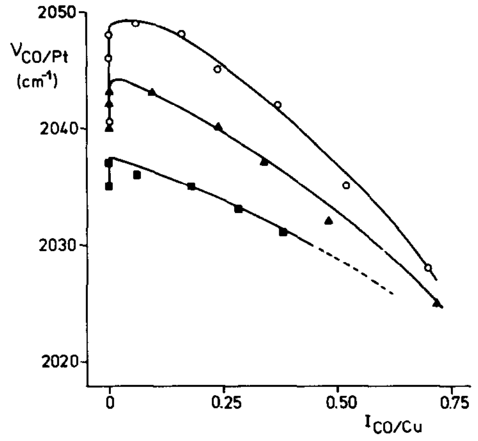

FIG. 2. Wavenumbers of the ir absorption band maxima of CO adsorbed on Pt in the Pt–Cu 42–58 alloy as a function of the height (in extinction units) of the ir absorption band of CO on Cu. For isotopic mixtures the two heights are summed up (counted together). (○) ^{12}CO; (▲) ^{12}CO : ^{13}CO = 60 : 40; (■) ^{12}CO : ^{13}CO = 25 : 75.

does not play any role here; we compare mainly the values for θ(CO/Pt) → 1.) However, on alloys also a new phenomenon could be observed: the CO/Pt band frequency decreased again as soon as the CO/Cu band started to develop. This effect was reversible: when CO was desorbed from Cu by evacuation, the CO/Pt band regained its original frequency. In Fig. 2 the CO/Pt band frequency is plotted against the intensity of the CO/Cu band. This intensity is related to the surface coverage of CO on Cu. All alloys showed essentially the same behavior in this respect. Figure 2 also demonstrates that the size of this effect is reduced by isotopic dilution.

The average particle size of all alloys on Al_2O_3 as determined with electron micrographs was about 20 Å. As a consequence, it was not possible to obtain X-ray diffraction data with these powders. It is therefore important to compare the data with those obtained with the alloys on SiO_2 where the presence of single-phase alloys could easily be established from the X-ray diffraction data. This comparison is shown in Fig. 3. As can be seen, the agreement between the two sets of data is quite satisfactory. We consider the continuous shift of the CO/Pt band frequency upon varying alloy composition and the absence of separated CO/Pt peaks as a strong indication for the formation of one-phase alloys also on Al_2O_3. Otherwise, in this range of sizes the difference in particle size does not seem to have a great influence on the frequency of the ir absorption band of CO adsorbed on these alloys.

The frequency values of the high-frequency band of several isotopic mixtures for pure Pt and the three alloys on Al_2O_3 are shown in Fig. 4. In spite of a certain scatter in data, it is clear that the effect of Cu on the CO/Pt frequency is most pronounced with pure ^{12}CO; a dilution by ^{13}CO leads to

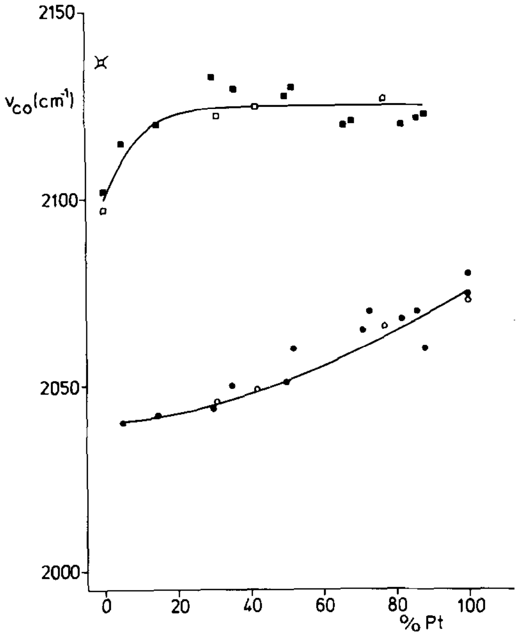

FIG. 3. Wavenumbers of the ir absorption band maxima of adsorbed CO as a function of alloy composition, at constant coverage by CO. (■) CO/Cu on SiO_2; (□) CO/Cu on Al_2O_3; (●) CO/Pt on SiO_2; (○) CO/Pt on Al_2O_3.

a strong decrease of this effect. Extrapolation of all curves results in an "isolated ^{12}CO frequency" of 2034 ± 3 cm^{-1}.

The frequency of CO adsorbed on unalloyed Cu is clearly influenced by the carrier, in contrast to alloys and pure Pt. CO adsorbed on Cu/SiO_2 revealed a well-developed single absorption band around 2100 cm^{-1} which shifted to lower frequencies upon isotopic dilution. Such behavior can be expected for metallic Cu[18]. However, CO adsorbed on Cu/Al_2O_3 prepared and treated in the same way as Cu/SiO_2 only showed a very weak band around 2130 cm^{-1}. Only if calcination in air at 600°C had been performed before the first reduction were bands of "normal" intensity obtained: there was a major band at 2097 cm^{-1} with a satellite at 2137 cm^{-1}. Upon isotopic dilution only the former shifted to lower frequencies (see Fig. 5).

In contrast with this, the band of CO on Cu in the *alloys* on Al_2O_3 did not behave differently from those on SiO_2. As can be seen in Fig. 3, a single band is always observed for the CO/Cu band between 2120 and 2130 cm^{-1}. From Fig. 5 it is clear that the position of this band is hardly influenced by isotopic dilution.

A last experimental point to be mentioned concerns the transfer of intensity from the low-frequency to the high-frequency band. From Fig. 1 it is already obvious that this phenomenon, clearly observable on pure metals, is strongly reduced by alloying. In Fig. 6 we have plotted the transfer in the CO/Pt bands for two isotopic ratios as a function of the bulk composition of the alloys. It is obvious that the transfer decreases upon decreasing content of ^{13}CO in the adsorption layer or increasing content of Cu in the alloy. Furthermore, the transfer proved to be insensitive to the gas phase pressure, i.e., to the presence or absence of CO on Cu.

DISCUSSION

The data presented in Figs. 1 and 3 fully confirm our earlier findings with Pt–Cu alloys concerning the effects of alloying on the ir spectra of adsorbed CO (*24*). Apparently, it does not make too much difference whether SiO_2 or Al_2O_3 is used as a carrier for the alloys.

Various mechanisms have been proposed in the literature to explain the effects of alloying on the ir spectra of adsorbed CO. Until now, most if not all authors believed that the observed frequency shifts could be fully explained by some changes in the electronic structure of the metals, for example, by a shift of electrons from, say, Cu to Pt (see also the Introduction). In such an explanation both frequency shifts of the CO/Cu and CO/Pt bands are assumed to be caused by changes in the extent of back-donation.

We did not find this a very likely explanation because, *inter alia,* it is well known that the back-donation is much less important on Cu than on Pt. Therefore, we sug-

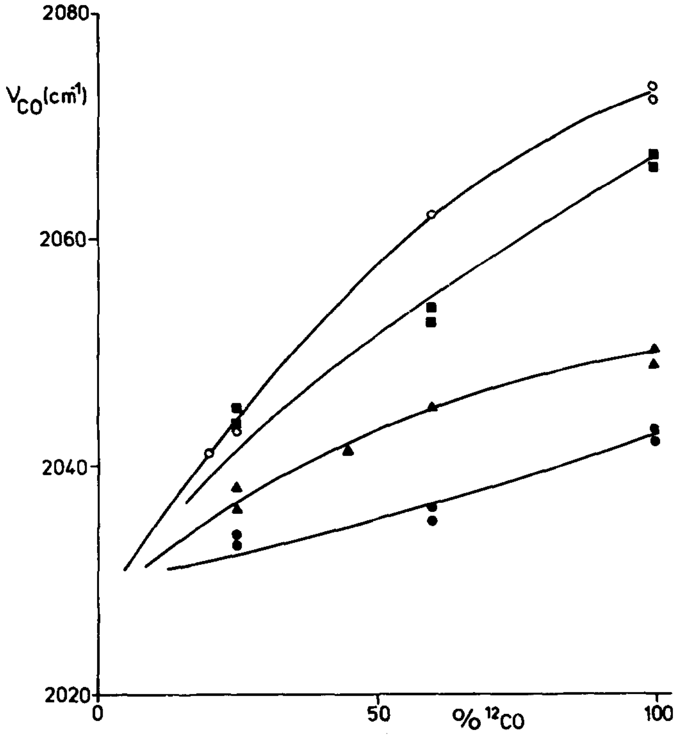

FIG. 4. Wavenumbers of the high-frequency "^{12}CO" ir absorption band maxima of CO adsorbed on Pt as a function of isotopic composition. All samples supported on Al_2O_3, at constant coverage by CO. (○) Pt; (▲) Pt–Cu 76–24; (■) Pt–Cu 42–58; (●) Pt–Cu 31–69.

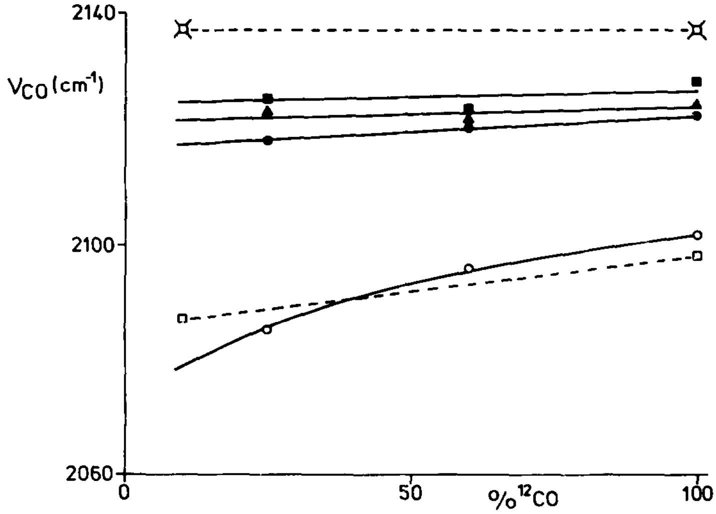

FIG. 5. Wavenumbers of the high-frequency "^{12}CO" ir absorption band maxima of CO adsorbed on Cu as a function of isotopic composition. (□) Cu on Al_2O_3; (⌑) Cu (satellite peak) on Al_2O_3; (●) Pt–Cu 31–69; (■) Pt–Cu 42–58; (▲) Pt–Cu 76–24; (○) Cu on SiO_2.

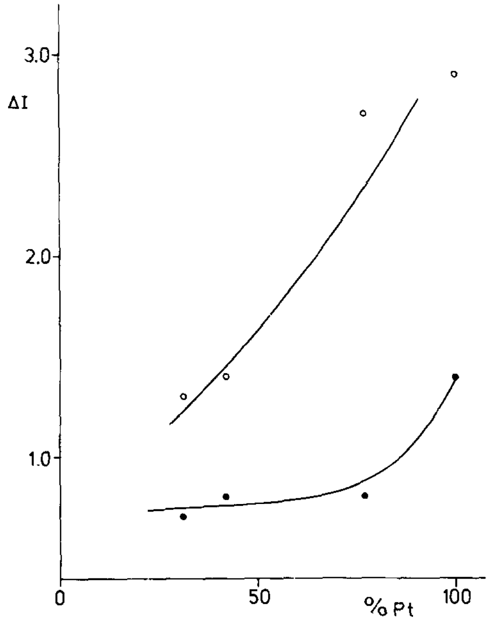

FIG. 6. Transfer of intensity from the low-frequency to the high-frequency band CO/Pt in the adsorption of isotopic mixtures as a function of alloy composition. The transfer defined as:

$$\Delta I = \frac{I(^{12}CO)}{I(^{13}CO)} \times \frac{\%(^{13}CO)}{\%(^{12}CO)}$$

in which $I(^{12}CO)$, $I(^{13}CO)$ = the heights of the respective ir absorption bands in extinction units and $\%(^{12}CO)$, $\%(^{13}CO)$ = the respetive mole ratios (in %) in the isotopic mixtures. (○) $^{12}CO:^{13}CO = 25:75$; (●) $^{12}CO:^{13}CO = 60:40$.

gested in an earlier paper (*24*) an alternative explanation based on an effect of "individualization" of the Pt and Cu atoms in the alloy. The result of this effect would be an increase of both direct and back-donation. The effect of back-donation on the frequency for the CO/Pt band is larger than the effect of direct donation. The opposite is true for the CO/Cu band where an upward shift due to alloying was predicted.

A third effect is also mentioned in the literature, as in our own previous paper (*24*), but regarded as being of minor importance and, apparently, explaining only the downward shift of the CO/Group VIII-metal ir absorption band. This is the essentially geometric effect of the dilution of the layer of interacting dipoles. As already mentioned in the Introduction, parallel vibrating dipoles will encounter a repulsive interaction and vibrate with an increased frequency; this effect is largest for dipoles with an equal frequency in the absence of coupling. This means that CO molecules adsorbed on Pt in an alloy will encounter (at $\theta_{CO/Pt} \to 1$) less coupling than on the pure metal under otherwise the same conditions. In our earlier paper (*24*) we *underestimated* this effect. The reason for this was that with pure Pt/SiO_2 we observed smaller variations of the frequency ν(CO/Pt) with the surface coverage θ(CO/Pt) than with alloying. Our conclusion therefore was that (i) the dipole–dipole coupling was less important on the supported metals than on the flat surfaces of single crystals or films (*14, 24*), and (ii) it should not be responsible for the observed shift upon alloying. However, this appears to be a poor argument, as the data of this paper show.

Crossley and King (*16*) have shown that on a more open single crystal plane of Pt, CO tends to cluster already at a low surface coverage. Through this, the ν(CO/Pt) frequency is high already at θ near to $\theta \to 0$ and it increases less with increasing θ. Also observations by Reinalda and Ponec (*25*) confirmed a picture of the possibility of CO clustering with evaporated films of Ir. In order to check the influence of clustering on the $\nu(\theta)$ curves, we have reinvestigated the adsorption of CO on various supported metals using the isotopic dilution method (*26*). The most relevant result was as follows: the variation of ν(CO/Pt) with increasing dipole–dipole coupling is *large enough* to account for the effect of alloying Pt with Cu. Clustering of CO occurs on powders already at the lowest θ(CO/Pt) and deforms the $\nu(\theta)$ curve. This leads to an apparently low effect of θ on ν(CO/Pt).

An estimate of the size of the geometric dilution effect of Cu on the CO/Pt band frequency could only be obtained by the isotopic dilution method, as described in the Introduction. The results are assembled in

Fig. 4. The conclusion is obvious and straightforward: within the accuracy of our experiments *the effect of Cu is mainly geometric, a dilution* of the CO/Pt layer. All curves converge to practically the same point and there seems to be very little, if any, room left for an "electronic structure (ligand)" or "individualization" effect. Evidently, alloying Pt by Cu does not change the bond strength of the C–O bond. In view of this, we feel that many results in the literature that have been ascribed so far to a ligand effect should be explained partially or even fully by a geometric effect of dilution. There is no reason to expect the features of the electronic structures of comparable alloys to be fundamentally different from those of Pt–Cu. The reported ir frequency shifts for Ni–Cu (*27*), Pd–Ag (*28*), Pd–Au (*29*), and Rh–Cu (*30*) are all between 15 and 30 cm^{-1}, values within the range to be expected for (varying) dipole–dipole coupling; since all those alloys are formed less exothermically than Pt/Cu alloys, the $\Delta\nu$ shifts in Refs. (*27–30*) should be ascribed to a geometric rather than to an electronic effect. Ligand effects will probably not play an important role in these alloys. The reactivity of the C–O bond with respect to dissociation or hydrogenation, etc., is therefore *not* changed by any ligand effect. Any changes in the chemical behavior of CO adsorbed on these or similar alloys should be ascribed primarily to geometric (ensemble size) effects. However, at the same time we do not want to exclude the possibility of an observable ligand effect with alloys which are formed more exothermically than Pt/Cu, such as, for example, Pt/Pb and Pt/Sn alloys. Investigations in this direction are in progress.

So far we have been concerned with the most important conclusion of this paper. However, the results of this study allow a discussion on some other points as well.

An interesting phenomenon observed in our experiments on alloys is the variation of the CO/Pt band frequency with the surface coverage by CO of the Cu sites. From Fig. 2 it is clear that this frequency is reduced upon increasing θ(CO/Cu). Two reasons can be responsible:

(1) The CO molecules on Cu donate electrons to Cu and by that also to Pt (an adsorbate–ligand effect). In principle this is possible because the direct donation from CO to Cu is more important than the back-donation (cf. work function measurements (*31*)). The extra electrons in Pt would increase the back-donation to CO/Pt and thus reduce ν(CO/Pt).[3]

(2) The CO/Cu molecules are screening the dipole–dipole interaction between the CO/Pt molecules.

Again, the isotopic dilution experiments offer the means to discriminate between these two possible effects. If the first explanation were true, it would make no difference; the extra effect of CO adsorbed on Cu should be the same in magnitude whether the observed ^{12}CO/Pt molecule is situated in a ^{12}CO/Pt or in a ^{13}CO/Pt matrix. The real shift should be the same for these two extreme cases. However, in the case of the second explanation, it would make a difference: if the "observed" ^{12}CO/Pt molecule is already decoupled from the ^{12}CO molecules by ^{13}CO/Pt then the CO/Cu molecules would have no additional decoupling effect. This means that the mentioned downward frequency shift should become smaller upon increasing the content of ^{13}CO. It is clear from the results of the isotopic experiments, collected in Fig. 2, that this is indeed the case. Therefore, although the first explanation cannot be fully excluded, the second is to be preferred.[4]

The frequency of the ir absorption band of CO adsorbed on Cu is a less reliable source of information on bonding than the frequency ν(CO/Pt). In the literature, val-

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[3] Note the difference with the "electronic effect" mentioned above, where the electrons originate from Cu itself (a metal–ligand effect).

[4] This mechanism of screening may also be the reason why in Ref. (*15*) the curves of ν_{CO} with θ and with percentage ^{12}CO do not fit, although clustering cannot be excluded either.

ues between 2095 and 2145 cm^{-1} have been reported for CO adsorbed on supported Cu (*26, 32, 33*). Apparently, two factors can be responsible for this large scatter: (i) The presence of variations in the particle size and in the degree of reduction. According to de Jong *et al.* (*33*), very small Cu particles (the authors speak about a few or even isolated Cu atoms on the carrier) give rise to relatively high frequencies (~2140 cm^{-1}) upon CO adsorption. This is analogous to the results obtained from matrix isolation techniques by Moskovits and Hulse (*34*). (ii) The presence of oxygen on the surface generally causes an increase in the frequency (*35*).

A tentative band assignment of our results with pure Cu on carriers is then as follows. The ir band around 2100 cm^{-1} is most probably due to CO adsorption on well-reduced particles which are not too small. The satellite at 2137 cm^{-1} found with Cu/Al_2O_3 should then be ascribed to adsorption on "single Cu atoms" or on oxidized Cu.

It is well known that the adsorption strength of CO on oxidized Cu is larger than on reduced Cu (compare Refs. (*18*) and (*36*)). We found that this is indeed true: after pretreatment of Cu/Al_2O_3 by O_2, the CO/Cu band disappeared clearly more slowly upon evacuation than after pretreatment by H_2. Therefore, the desorption characteristics are indicative for the degree of reduction. As already mentioned, after pretreatment by H_2 the Cu/Al_2O_3 sample revealed a band at 2097 cm^{-1} and a satellite at 2137 cm^{-1}. Both these bands disappeared fast and with equal speed upon evacuation. The satellite can therefore be identified most probably as caused by adsorption of CO on very small Cu clusters. This assignment is also compatible with the observed absence of a frequency shift of this band upon isotopic dilution (see Fig. 5). So far, on pure Cu/support powders.

When Cu is alloyed with Pt only one ir absorption band of reasonable intensity (see Fig. 1) and of a frequency between 2120 and 2130 cm^{-1} is found, independent of the carrier material (see Fig. 3). Again, one could wonder if this higher frequency ν(CO/Cu) has not been caused by an incomplete reduction of Cu in the alloys. However, desorption experiments clearly showed a picture of reduced Cu. After pretreatment of the sample by O_2 the band was disappearing more slowly upon evacuation. We are therefore confident that Cu in the presence of Pt is fully reduced.

One may ask then which effects are responsible for the experimentally observed frequencies. The answer can probably be derived from Fig. 5. There is almost no frequency shift observable with isotopic dilution, just as for the satellite observed on Cu/Al_2O_3. It seems therefore probable that the CO-on-Cu molecules in the alloys are also "isolated." The difference in frequency with the ν(CO/Cu) satellite frequency (~2125 cm^{-1} as compared with 2137 cm^{-1}) must then be ascribed to the different matrices in which these "isolated" atoms are placed, viz. Al_2O_3 vs Pt.

The reason for the increase in the frequency of adsorbed CO upon "isolation" of Cu, can probably be found in the bonding character of CO on Cu. The Cu 3*d*-orbitals are completely filled and will not play an important role in the bonding. Because of the geometry of the metal *sp*-orbitals, back-donation from them will be less important than from the *d*-orbitals of the Group VIII metals. Therefore, the bond of CO to Cu is formed mainly by a donation of electrons from the slightly antibonding 5σ-orbitals of CO into the metal *sp*-orbitals. This direct donation strengthens the C–O bond and increases the frequency. Any effect which would increase this direct donation could be responsible for the results collected in Fig. 3. A shift of electrons from Cu to Pt would be such an effect. However, it is not a plausible explanation. First, we did not observe the reverse effect on ν(CO/Pt) and second, XPS data do not reveal any shift of electrons (*37*). On the other hand, the XPS data show a rehybridization of the orbitals of Cu in the alloy. Such a rehybridization combined with the effect of individualization (an increase in the local densities of states at the atomic energy level due to band narrowing) of the Cu atoms may lead to an increased susceptibility of Cu for the donation of the 5σ-CO electrons. It should be noted here that upon alloying the local density of states increases. This is not in contradiction with a general decrease of the total density of states.

The next question to be answered is why a similar effect is not operating on Pt. The answer can again be found in the bonding of CO to the metals. On Cu the bonding is mediated mainly by the *sp*-electrons, whereas on Pt the *d*-electrons play also an important role. Since the *sp*-electrons are much more delocalized than the *d*-electrons, one can imagine that a disturbance of the metal (by alloying) will have a larger effect on the former than the latter. An increasing isolation of the Pt atoms, where the *d*-electrons are fairly "atomic" already in the state of a pure metal, will then have a much smaller effect. This explanation is consistent with all data available at the moment, but a deeper analysis is needed to explain the striking difference more fully.

Another effect to be commented on is the absence of the influence of the dilution by ^{13}CO on the frequency of the CO/Cu band in the alloys. This is even more surprising when one realizes that the surface of the alloys is probably enriched in Cu. On the other hand, even at relatively high gas phase pressures of CO, the surface of Cu is never completely covered. The coupling effect of CO/Cu will then presumably be lower than that of CO/Pt. However, the almost total absence of any frequency shift requires a further explanation. If we assume the dipole–dipole coupling to be a dynamic electromagnetic coupling-through-space, then the difference in bonding character of CO on Pt and Cu cannot account for the experimentally found difference. The most likely explanation can be extracted from Fig. 2. One can see there that the ^{12}CO/Pt–^{12}CO/Pt coupling is screened upon increasing surface coverage of CO on Cu. Analogously, we can expect CO/Cu to be screened by CO/Pt. Since the surface of Pt is already fully covered by CO before CO starts to be adsorbed on Cu, the CO/Cu molecules are to a large extent decoupled already from the start of the adsorption on Cu. The constant absorption band frequency of 2125 cm^{-1} is then not surprising.

The intensity transfer observed in the isotopic experiments (occurring from the low-frequency to the high-frequency band of CO/Pt) clearly decreases upon alloying Pt with Cu (see Figs. 1 and 6), just as the dipole–dipole coupling between the CO molecules adsorbed on Pt (see Fig. 4). Intensity transfer occurs because the various frequency modes of the whole layer have different dynamic dipole moments. ^{13}CO contributes to the resulting dipole moment of the in-phase ^{12}CO–^{13}CO vibrations at the ^{12}CO-like frequency, while ^{12}CO diminishes the resulting dipole moment of the ^{12}CO–^{13}CO out-of-phase vibrations at the ^{13}CO-like frequency (compare this with the analyses by Decius (*38*) or Persson and Ryberg (*20*)). The size of this effect is inversely proportional to the distance between the absorbing species. It is not surprising, therefore, that alloying Pt by Cu causes both a decrease of the dipole–dipole coupling as well as of the intensity transfer ΔI. However, this does not mean that one is proportionally varying with variations of the other. For example, an increase in the dilution by ^{13}CO decreases the dipole–dipole coupling between the ^{12}CO molecules but increases the intensity transfer at the same time (cf. the two curves in Fig. 6). Further, the presence of CO on Cu clearly reduces the dipole–dipole coupling (see Fig. 2) but had no effect on the intensity transfer.

Finally, we have made an attempt to estimate the surface composition of our alloys from the ir absorption band frequency data. The general idea behind this is as follows. If

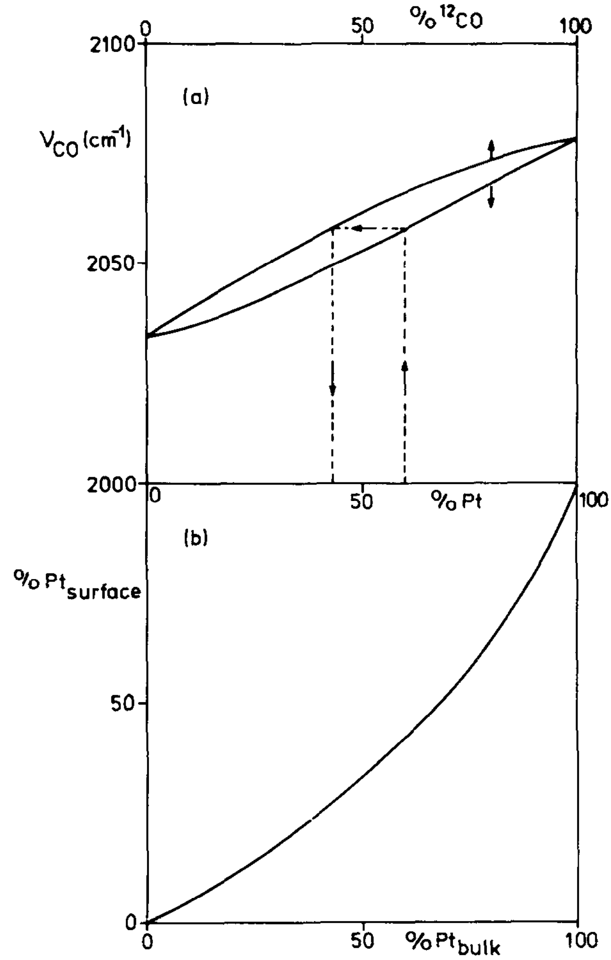

FIG. 7. Correlation of the wavenumbers of the ir absorption band maxima of CO adsorbed on Pt with the alloy composition of the Pt–Cu system on SiO_2 or Al_2O_3. (a) Upper curve: equal to that in Fig. 4 for Pt. Lower curve: equal to that in Fig. 3 for Pt. The arrows indicate which bulk composition would match the corresponding surface composition. (b) Surface vs bulk composition as determined from (a).

we compare the curves of the frequency of the ^{12}CO/Pt band plotted (i) as a function of the isotopic composition on unalloyed Pt and (ii) as a function of the bulk composition of the alloys, we can see in Fig. 7a that these curves do not coincide. Nevertheless, we have proved that Cu should have almost the same diluting effect on the CO/Pt band frequency as does ^{13}CO. The reason for this discrepancy is obviously the difference between the surface and bulk composition of the alloys. The surface composition of the alloy can now be easily deduced from these curves, in the way indicated in Fig. 7a by arrows. The plot of surface against bulk composition determined in this way is shown in Fig. 7b. Preliminary Auger data (*39*) obtained with equilibrated Pt/Cu alloys showed a similarity with this curve.

To sum up, the work as a whole leads to the following conclusions:

(1) The shift of the absorption band frequency of CO adsorbed on Pt upon alloying with Cu is mainly caused by the diluting effect of alloying; a ligand effect on the ir spectra has not been observed within the accuracy of our experiments.

(2) The results can be understood by

means of the theory developed for dipole–dipole interactions.

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