JOURNAL OF CATALYSIS 64, 110–115 (1980)

Adsorption of CO on Pt–Cu Alloys. On the Possible Role of Atomic and Collective Properties of Metals in Chemisorption: Observations by Infrared Spectroscopy

F. J. C. M. TOOLENAAR, D. REINALDA, AND V. PONEC

Gorlaeus Laboratoria, Rijksuniversiteit Leiden, Postbus 9502, 2300 RA Leiden, The Netherlands

Received June 18, 1979; revised October 11, 1979

A series of Pt–Cu alloys on a silica carrier has been prepared and investigated by infrared spectroscopy. It is observed that the position of the infrared bands is a function of the alloy composition. Comparison of the data obtained with other systems reported in the literature excludes the explanation of the shift in terms of electron transfer between alloy components (changes in n_d, the number of *d* electrons) or in terms of bond strength to the nearest neighbors of the metal atoms in alloys. A tentative explanation is suggested according to which changes in the collective properties of metals (local density of states) are responsible for the shift of the infrared band maxima.

I. INTRODUCTION

The catalytic and chemisorptive behavior of alloys has already been a matter of considerable interest for many years. The work on fundamental problems intensified recently when it appeared that alloys (or more general bimetallic catalysts) could be superior to pure metals as far as their practical use is concerned (for reviews, see Refs. (*1–3*)).

The main result that emerged from all of the fundamental studies was that the effect of alloying consisted mainly in reducing the "ensembles" of active sites that are necessary for some types of adsorption of hydrocarbons (*1–6*) or carbon monoxide (*7, 8*). Although in many alloy systems the changes in the electronic structure due to alloying are not very pronounced (*1–6*), it has nevertheless always been expected that they might influence some features of the chemisorption layers sufficiently to be detected.

It is also desirable to know which chemisorption properties are determined by the "atomic" properties of metallic elements and which are dependent on the collective properties of metals. From other literature data (*9, 10*) it is clear that infrared spectroscopy might be a sensitive probe to attack the problems that concern alloying and chemisorption behavior.

This investigation deals with the adsorption of CO on Pt, Cu, and Pt–Cu alloys, all supported on silica. Using also literature data on similar alloy systems, an explanation of the results is presented, based on considering the atomic and collective properties of the metals investigated.

II. EXPERIMENTAL

The preparation of pure Pt- and Cu-on-silica catalysts proved to be rather easy: the best results, viz., yielding the smallest particles, were obtained using precipitation by urea (*11*) from a solution of the metals on a high-surface-area silica (Aerosil 380). The particle size, as roughly estimated by X-ray diffraction line broadening, was about 30 Å for both Pt and Cu.

The preparation of a single-phase alloy on silica catalyst proved to be much more difficult and less predictable; as a consequence the alloys mentioned and used in this paper have not all been made in the same way. They were prepared either by impregnation or precipitation by urea, on

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different silica carriers (Aerosil 150, 300, or 380). Nevertheless, the results did not reveal any effect caused by varying conditions. The X-ray diffraction of all alloys reported in this paper showed a single phase and a particle size between 60 and 150 Å.

With pure Pt two samples were prepared with an average particle size of 30 and 200 Å, respectively. The shape and position of the CO band were almost the same for both powders and we believe therefore that the lack of control of particle size with alloys is no serious limitation to the comparisons we are making in this paper.

The bulk composition of the alloys has been determined by X-ay fluorescence. The exact surface composition of our Pt–Cu alloys is not known (to determine it, both the total surface area as well as that of one component should be measured). Rough estimates using ir band integrated intensities show that alloy surfaces are slightly enriched in Cu. Auger spectra of alloy powders, taking in our laboratory, showed also a rather low extent of Cu segregation in contrast with theoretical predictions. However, as we discuss in this paper only the band positions and not their intensities, no effort has been made to gain more accurate information.

After drying at 120°C, reducing under flowing hydrogen at 400°C and cooling to room temperature, a sample of about 50 mg was compressed (in air) into a disk at 2 tons/cm^2 pressure and placed into a glass cell with sealed-in Si-windows. The cell was connected to a high-vacuum system. After evacuation the pellet was reduced *in situ* under flowing hydrogen, at 350°C, for about 18 hr, evacuated for 1 hr while still hot, and then during cooling, until the pressure fell to about 10^{-5} Torr.

The infrared spectra were obtained with a Perkin–Elmer 325 spectrophotometer. The 2200- to 1900-cm^{-1} spectra were recorded 5 min after admission of the CO at pressures ranging from 10^{-3} to 10 Torr, at room temperature. The bands on Pt reach their maximum in the region of 10^{-3}–10^{-2} Torr, but the band on Cu does not reach saturation even at 10 Torr. At high pressures a gas-phase CO band appears as a distortion on the high-frequency side of the CO on Cu peaks; this gas-phase peak is subtracted from the spectra shown in Fig. 1. It should be mentioned further that another band is observed at about 1850 cm^{-1} on Pt and Pt-rich alloys. However, this is a very weak band that we could not analyze in the way we did in the region 2200–2000-cm^{-1}.

The transmission spectra produced by the spectrophotometer were converted into extinction units using the formula

$$E = \log(T_{\text{back}}/T_{\text{ad}}),$$

where E stands for extinction, T_{back} for transmission of the background, and T_{ad} for transmission with CO.

III. RESULTS

The main features of the infrared spectra converted into extinction units are presented in Fig. 1.

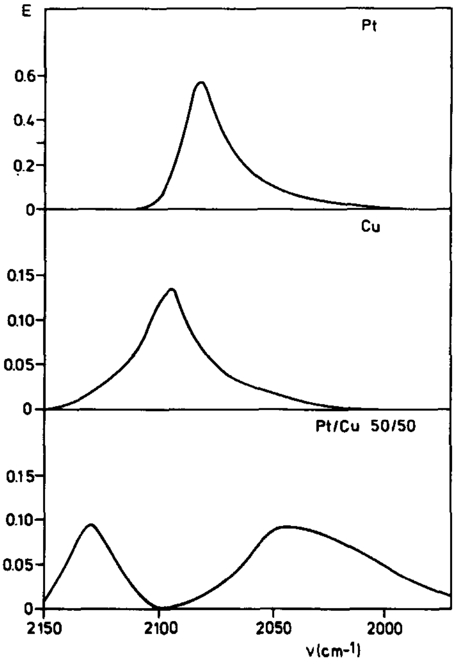

FIG. 1. Spectra of Co adsorbed on Pt, Cu, and Pt–Cu; p_{CO} = 10 Torr.

As can be seen immediately, CO adsorbed at 10 Torr on the pure metals reveals a single absorption band with $\nu_{\max}$ at 2085 cm^{-1} for Pt and at 2095 cm^{-1} for Cu. With increasing pressure (i.e., increasing surface coverage) a positive shift from 2070 to 2085 cm^{-1} for CO on Pt and a negative shift from 2098 to 2095 cm^{-1} for CO on Cu have been observed in the position of the infrared band.

The spectra of CO adsorbed on the Pt–Cu alloys at 10 Torr exhibit two absorption bands that shift to higher wavenumbers with increasing Pt content, one from 2040 to 2070 cm^{-1} and the other from 2105 to 2130 cm^{-1}. We assigned the first one to CO on Pt and the second one to CO on Cu for the following reasons: (i) it is well known from the literature that CO adsorbed on transition metals absorbs at lower wavenumbers than CO adsorbed on Ib metals; (ii) the spectra were taken in the presence of 10 Torr CO in the gas phase, and upon pumping only the 2105–2130 peak disappeared, which is characteristic for the weaker adsorption of CO on Cu; (iii) the relative peak areas revealed an increase for the 2040- to 2070-cm^{-1} band and a decrease for the 2105- to 2130-cm^{-1} band with increasing Pt content. From Fig. 2 a continuous shift of the CO-on-Pt band caused by alloying with Cu can be clearly seen. The variations of the $\nu_{\max}$ of CO on Cu upon alloying are less pronounced: there seems to be a clear shift to higher wavenumbers due to alloying, but beyond a certain value the $\nu_{\max}$ remains almost constant in a broad range of alloy compositions. No effect of particle size, carrier, or preparation method could be detected within the limited variations applied.

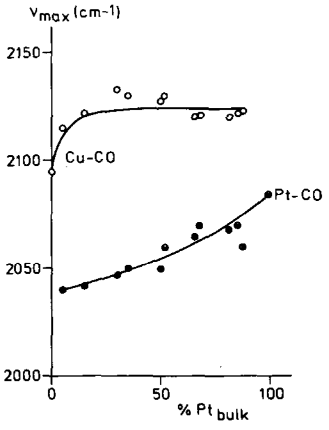

FIG. 2. Absorption band maxima of CO adsorbed on Pt (⊗) and Cu(○) as a function of alloy composition.

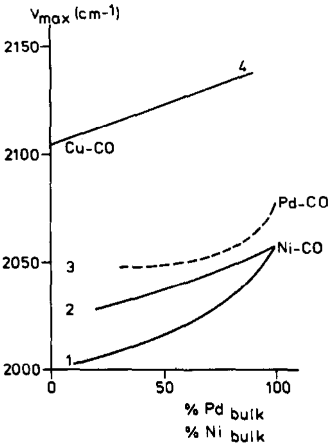

FIG. 3. Literature data on absorption band maxima of CO adsorbed on several alloys as a function of alloy composition (1) CO on Ni in Ni–Cu (*10*); (2) CO on Ni in Ni–CO (*14*); (3) CO on Pd in Pd–Ag (*9*); (4) CO on Cu in Ni–Cu (*10*).

IV. DISCUSSION

One conclusion is very straightforward: CO molecules adsorbed on transition or Ib metals are distinguishable also on alloys. In this respect metals preserve their identity given by the atomic properties of the elements, in a similar way to UPS and XPS spectra (for reviews, see Refs. (*4*, *5*)).

The data presented in this paper are in many respects similar to those obtained by other authors: Primet *et al.* (*9*) found that the $\nu_{\max}$ of CO on Pd decreased upon alloying with Ag (see Fig. 3); the fact that this $\nu_{\max}$ remains constant beyond about 50% Ag, whereas in Pt-Cu a more continuous decrease is observed, could be ascribed to a different surface composition of these alloys (*8*, *12*, *13*). Dalmon *et al.* (*10*) observed for Ni–Cu a decrease of the $\nu_{\max}$

of CO on Ni and a (continuous) increase for CO on Cu by alloying (see Fig. 3). Results obtained by Van Dijk (*14*) on Ni–Co indicated that the peak of CO on Ni shifts to lower wavenumbers upon alloying with a second transition metal like Co as well (see Fig. 3). Combining these results, it is therefore obvious that the $\nu_{\max}$ of the ir band of CO on transition metals *always* decreases by alloying while on Ni–Cu and on Pt–Cu an increase of the $\nu_{\max}$ of CO on the Ib metal is noted.

The alloys mentioned above form a suitable basis for discussion, as they comprise systems for which many parameters are different. The number of the transition metal d-electrons, n_d, varies for Pd–Ag but remains constant for Ni–Cu (*15*). The saturation magnetic moment (M) decreases for Ni–Cu, but increases for Ni–Co (*16*). There are alloys formed ($\Delta H_f{}^0 > 0$) endothermically (Ni–Cu) as well as alloys formed with a small (Pd–Ag) or moderate (Pt–Cu) exothermic effect (*17*). In Ni–Cu alloys the two components tend to form Ni and Cu clusters while in Pt–Cu short-range ordering of the Pt and Cu atoms is possible.

It can be seen immediately that the above-mentioned parameters (n_d, M, and ligand effects due to variations in $\Delta H_f{}^0$) cannot be responsible for the observed changes in $\nu_{\max}$ of CO adsorbed on transition or Ib metals by alloying, as these changes are always in the same direction. It is particularly noteworthy that the speculations on the variations in n_d (*18*), which were and in some cases still are very popular in the literature, cannot explain these data (compare Ni–Cu, Ni–Co, and Pd–Ag).

The position of the absorption band maximum $\nu_{\max}$ is a function of the surface coverage θ_{CO} (*19*), so a possible explanation can be that the shifts are caused by a variation in θ_{CO} with alloying.

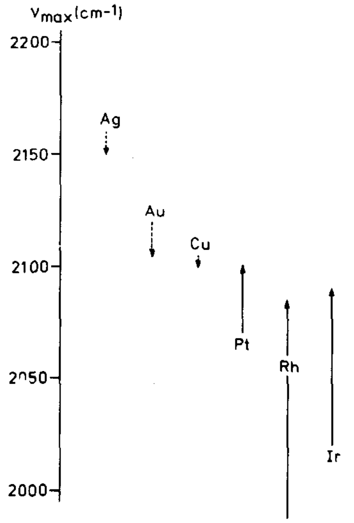

FIG. 4. Literature data on the variations of the ir band maxima of CO adsorbed on Ib (*20*) and transition (*21*) metals upon increasing surface coverage (for Cu our own results are considered).

As shown in Fig. 4, the $\nu_{\max}$ of CO on transition metals *increases* with increasing θ_{CO}, while on Ib metals a *decrease* is reported (*20, 21*). This is confirmed by our results on pure Pt and pure Cu. It has been established that the main mechanism responsible for the $\nu(\theta)$ shifts is coupling of vibrating dipoles (*19*). However, we may assume that CO molecules that exhibit a different frequency in their ir spectra do not influence each other by mutual coupling. This means that alloying will always have the same effect as lowering the surface coverage and the results presented in this paper could at least qualitatively be explained in this way. However, when we take the size of the effects into account a large discrepancy can be noticed. While the effects caused by a varying surface coverage of CO are usually very small on Cu (less than 5 cm^{-1}), the effects caused by alloying amount to between 20 and 30 cm^{-1}; for CO on Pt there seems to be a similar discrepancy also, although probably less pronounced. It should be noticed that when CO molecules with different frequencies in their ir spectra do influence each other, the discrepancy between surface coverage and alloying effects of CO on Cu becomes even greater because then diluting Cu with Pt would mean an increase of the effective surface coverage. While a part of the total

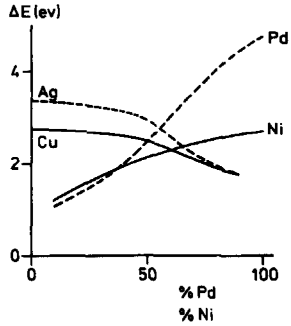

FIG. 5. Literature data (*22*) of the width of the *d*-band of all components of Pd–Ag (---) and Ni–Cu (——) as a function of alloy composition, as revealed by XPS experiments.

effect on $\Delta\nu_{\max}$ can be ascribed almost certainly to an increasing mutual distance of the CO molecules due to alloying (see Figs. 2 and 3), the question remains what additional effects may be operative next to it.

The position of the absorption band maximum $\nu_{\max}$ is a sensitive measure of the contribution to the bonding of "back-donation" of electrons from the metal *d*-orbitals into the π^* CO-orbitals. Back-donation, in turn, is sensitive to the vertical distance of CO from the surface, so that the shifts in $\nu_{\max}$ could have been ascribed to the changes in this distance occurring by alloying. However, from the above-mentioned data it is clear that variations in the radius of one of the components of an alloy have no reversal effect on the $\nu_{\max}$ shifts (compare Pt–Cu and Ni–Cu).

Having discussed all these possible explanations we arrive at one that is (so far) not contradicted by experiments. As can be seen in Fig. 5 the width of the *d*-band in XPS emission spectra decreases for all components of bimetallic systems by alloying (*22*), which means that the local $N(E)_d$ is higher in alloys. Although a similar effect on the width of the *sp*-band cannot be detected by XPS, similar behavior may be expected on theoretical grounds (*24*), namely, the bandwidth is dependent on the position of the atomic energy levels and on the overlap of orbitals when a metal is formed from the atoms. Making an alloy solution always causes a decrease of the bandwidth of all bands; only with very exothermically formed intermetallic compounds is a band broadening sometimes observed. Our suggestion is to relate this narrowing to the finding that the $\nu_{\max}$ of CO on an Ib metal increases upon alloying while it decreases on transition metals.

A semiempirical description (*23*) of charge transfer complexes like CO on transition metals reveals that the bond strength and the ability to transfer electrons in any direction are enhanced when the density of states is higher. While the effects on the heat of adsorption might be too small to be detected by calorimetric measurements, the $\nu_{\max}$ of CO on these metals is a more sensitive function of changes in the electron transfer (direct and back-donation). An increase in the density of states ($N(E)_d$ and $N(E)_s$) improves the conditions for electron transfer in both directions, but evidently to a different extent. Back-donation decreases the C–O bond strength and thus the stretching frequency $\nu_{\max}$, while direct donation from the nonbonding orbital (5σ) of CO has the opposite effect. On transition metals where back-donation is decisive for the position of the ir band, the effect of improving charge transfer in both directions will result in a net decrease of $\nu_{\max}$. With Cu the back-donation effect is much smaller and the direct donation effect evidently prevails here (changes in $N(E)_s$ are expected to be responsible for that) as a net increase of $\nu_{\max}$ is observed. A red shift with respect to free gas-phase CO molecules does not necessarily mean an indication of strong back-donation, but may also be caused by dipole–image dipole interactions. The Cu *d*-electrons are more contracted to the nucleus than with Ni or Pt, e.g., so that less back-donation must be expected also on theoretical grounds. The work function changes observed with Cu do not suggest strong back-donation effects either.

If our explanation is correct, the data presented and reviewed in this paper form an example of how the collective properties (density of states) interfere with the atomic states in determining the spectral behavior of CO on metals.

REFERENCES

1. Ponec, V., *Catal. Rev. Sci. Eng.* **11**, 41 (1975).
2. Clarke, J. K. A., *Chem. Rev.* **75**, 291 (1975).
3. Sinfelt, J., *Accounts Chem. Res.* **10**, 15 (1977).
4. Ponec, V., *in* "Electronic Properties on Metal Surfaces" (E. G. Derouane and A. A. Lucas, Eds.), p. 537. Plenum, New York, 1976.
5. Ponec, V., *in* "Progress in Surface and Membrane Science," Vol. 13 (C. Danelli and D. A. Cadenhead, Eds.). Academic Press, New York, 1979.
6. Ponec, V., *Int. J. Quantum Chem.* 12(2), 1 (1977).
7. Soma-Noto, Y., and Sachtler, W. M. H., *J. Catal.* **32**, 215 (1974).
8. Kuijers, F. J., and Ponec, V., *J. Catal.*, **60**, 100 (1979).
9. Primet, M., Mathieu, M. V., and Sachtler, W. M. H., *J. Catal.* **44**, 324 (1976).
10. Dalmon, J. A., Primet, M., Martin, G. A., and Imelik, B., *Surface Sci.* **50**, 95 (1975).
11. Geus, J. W., Dutch Patent Application 6705259 (1967).
12. Kuijers, F. J., thesis, Leiden (1978).
13. Kuijers, F. J. and Tieman, B. M., private communication on Auger spectra of Pt–Cu alloys.
14. Van Dijk, W. L., M.Sc. thesis, Leiden (1974).
15. Wenger, A., and Steinemann, S., *Helv. Phys. Acta* **47**, 324 (1974); Hoare, F. E., and Yates, B., *Proc. Roy. Soc. London Ser. A* **240**, 42 (1957); Stocks, G. M., Williams, R. W., and Faulkner, J. S., *J. Phys. F.* **3**, 1688 (1973); McLachlan, A. D., Jenkin, J. G., Leckey, R. C. G., and Liesegang, J., *J. Phys. F.* **5**, 2415 (1975); Crangle, J., and Hallam, G. C., *Proc. Roy. Soc. London Ser. A* **272**, 119 (1963).
16. Gibb, T. R. P., Jr., McMillan, J., and Roy, R. J., *J. Phys. Chem.* **70**, 3024 (1966).
17. Kubaschewski, O., and Caterall, J. A., "Thermodynamic Data on Alloys," Vol. 3. Pergamon, London, 1956; Elford, L., Müller, F., and Kubaschewski, O., *Ber. Bunsenges. Phys. Chem.* **73**, 601 (1969).
18. Blyholder, G., *J. Phys. Chem.* **68**, 2772 (1964).
19. Moskovits, M., and Hulse, J. E., *Surface Sci.* **78**, 397 (1978); Scheffler, M., *Surface Sci.* **81**, 562 (1979).
20. Bradshaw, A. M., and Pritchard, J., *Proc. Roy. Soc. London* **316**, 169 (1970).
21. Shigeishi, R. A., and King, D. A., *Surface Sci.* **58**, 379 (1976); Reinalda, D., thesis, Leiden, 1979.
22. Hüfner, S., Wertheim, G. K., and Wernick, J. H., *Phys. Rev. B* **8**, 4511 (1973).
23. Grimley, T., *in* "Molecular Processes on Solid Surfaces" (E. Drauglis, R. D. Gret, and R. J. Jaffee, Eds.), p. 299. McGraw-Hill, New York, 1969.
24. Kittel, J. C., "Introduction to Solid State Physics," 5th ed. Wiley, New York, 1976.