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Infrared Spectra of Carbon Monoxide Adsorbed on Supported Palladium and Palladium–Silver Alloys

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Infrared spectra of carbon monoxide adsorbed on supported Pd–Ag alloys were investigated. CO is strongly chemisorbed only on the Pd atoms. The infrared spectra provide information of the relative abundance of diadsorbed (=bridge bonded) and monoadsorbed (=linear) CO (of importance for the "ensemble effect" of alloy catalysts); they also show to what extent the band frequency depends on the chemical nature of the metal atoms adjacent to the adsorbing Pd atom ("the ligand effect" of alloy catalysts).

Three CO absorption bands were observed on Pd and on the alloys at ~2060, 1960 and 1920 cm^{-1}. The most marked result is that the band frequency remains almost constant for Pd and Pd–Ag alloys, but the relative intensities change in a very drastic manner. The 2060 cm^{-1} band which is ascribed to the linear CO complex and is rather weak for CO on Pd becomes the most important feature of the spectrum of CO on Pd–Ag alloys where the bands characteristic for bridged CO are very faint. It thus appears that for this system the geometric "ensemble effect" is more pronounced than the "ligand effect." We further conclude that Eischens' assignment of CO bands on transition metals is correct.

INTRODUCTION

One of the most spectacular discoveries in heterogeneous catalysis during the last decade is the marked effect of alloying on the catalytic selectivity of metal catalysts. Even for binary alloys AB where A is an element of high catalytic activity while B is inactive for the reaction considered, the selectivity can differ markedly from that of the pure metal A.

In previous publications from this laboratory it was shown that this phenomenon can in principle be ascribed to two causes (*1*):

a. The geometric "ensemble effect" (*2*, *3*). An adsorbing molecule can form chemical bonds with either one or with two or more surface atoms. Upon further reaction, each of these chemisorption complexes will lead to different reaction products. Diluting the adsorbing metal atoms with inert atoms will then change the selectivities in a predictable manner since the relative concentration of ensembles with a smaller number of atoms capable of forming chemisorption bonds will increase upon alloying with an inactive metal.

b. The electronic "ligand effect" (*4*). Even for a chemisorption bond between one metal and an adsorbed atom, the chemical nature of the neighbors of the adsorbing metal atom will be of importance. This ligand effect is familiar in the chemistry of metal-organic coordination complexes. As it is clear that catalytic selectivity is often determined by the relative chance of an adsorbed intermediate either to react further or to be desorbed, it is obvious that weakening the adsorption bond by alloying can in principle change selectivity.

While the existence of these two phenomena and their common responsibility for the selectivity effects caused by alloying seems to be generally accepted, there is very little evidence on the relative quantitative importance of each effect. We have therefore asked ourselves the following questions:

1. Is it possible to determine experimentally to what extent a molecule which is diadsorbed on a certain metal becomes monoadsorbed on an alloy when the metal is diluted with a nonadsorbing element?
2. Can the change in the nature of a chemisorption bond caused by alloying be identified by studying the infrared spectra of the adsorption complex on a pure metal and alloy or by characterizing the bond strength by a temperature programmed desorption?

Obviously it would be desirable to study both problems simultaneously on the same adsorption system.

This paper reports on the results of experiments carried out to answer these two questions which we consider of fundamental importance for catalysis by alloys. We selected the Pd–Ag alloy system for various reasons: Pd strongly adsorbs carbon monoxide, hydrogen, hydrocarbons, etc., under circumstances where the adsorption of these molecules on Ag is negligible. While such a specificity also holds for, e.g., Cu–Ni or Au–Pt alloys, the Pd–Ag system has the additional advantage that its heat of alloy formation is very small. As a consequence, the solid solution is stable at temperatures below those where Cu–Ni and Au–Pt are known to form two phases (*5*, *6*). The advantage of using a one-phase alloy for the present objective is that the surface composition can in principle be varied over the full range of 100% Pd–100% Ag. Another reason to select Pd–Ag is that the surface properties of this alloy have been studied by Bouwman, Lippits and Sachtler (*7*), Whalley, Thomas and Moss (*8*) and by Christmann and Ertl (*9*).

The choice of CO for the present work is also obvious. Besides the specificity of strong chemisorption by transition metal atoms, CO has the advantage of an exceptionally large infrared extinction coefficient, decisive for spectroscopic studies. Most important, however, is the strong evidence that for CO the diadsorbed "bridge complex" can be distinguished from the monoadsorbed "linear complex" by their different infrared absorption bands. On pure Pd the bridge complex prevails.

The assignment of the main bands in the spectrum of chemisorbed carbon monoxide was originally made by Eischens (*10*), and Eischens, Francis and Pliskin (*11*) who ascribed the bands below 2000 cm^{-1} to the bridge complex while the bands above 2000 cm^{-1} were assigned to the linear complex. However, this assignment became a matter of dispute when Blyholder (*12*) proposed a different interpretation which assumed that all bands corresponded to linear complexes and that different "electronic" configurations of the adsorbing metal atoms were assumed to be responsible for marked frequency shifts.

An analysis of this controversy shows that the present work on alloys should be capable of settling the dispute, as the two assignments lead to different predictions of the infrared spectrum of CO on diluted Pd–Ag systems. This consideration is elaborated in the Discussion section and has provided additional motivation for the present study.

Adsorption of CO has been measured quantitatively by a volumetric method. The rate of decrease in CO band absorbance by the desorption at prefixed temperatures was measured to provide data on the free energy of desorption which was important with regard to the ligand effect. As with all studies with supported alloys, the determination of the alloy surface area and the homogeneity of particle composition pose problems. In the present work the alloy particle sizes and their distribution were determined by electron microscopy. X-Ray line broadening was also used, but as the X-ray lines for alloys are also broadened by inhomogeneous particle compositions, the lines for alloys are used only to obtain an impression of the scattering of composition over the particles.

In order to estimate the extent of the electronic "ligand effect" on the infrared spectra of adsorbed CO from another direction, we finally included some spectroscopic work, where CO was adsorbed on Pd saturated with adsorbed hydrogen.

EXPERIMENTAL METHODS

Preparation of the Catalysts

Alloy catalysts supported by silica were prepared from palladium and silver nitrates. Silica (Aerosil HS-5) was impregnated with the mixed nitrate solution and dried. The catalysts were reduced in flowing hydrogen at 430°C for 6 hr. All alloy catalysts contained 9 wt% of metals. The metal composition was in the range of 97.5 at% Pd to 38.9 at% Pd. Supported Pd catalysts were prepared from several kinds of solutions, namely:

a. Pd metal plates dissolved in concentrated nitric acid (P_{14}).

b. Palladium nitrate solution prepared from $PdCl_2$ and $AgNO_3$ followed by filtering to remove AgCl.

c. $PdCl_2$ solution (P_{13}).

d. $Pd(NH_3)_4(NO_3)_2$ solution prepared by mixing ammonium solution to $Pd(NO_3)_2$ (P_{18},P_{16}).

The impregnation procedure was the same as that for the alloy catalysts.

Measurement of Infrared Spectra

The cell for spectral measurement was similar to that described earlier (*13*). Before the measurement the catalyst disc again was reduced in flowing hydrogen at 330°C for 1.5–2 hr and evacuated for 2 hr at the same temperature in the infrared cell.

Carbon monoxide was adsorbed at room temperature in the pressure range between 10^{-4} and 10 Torr.

A Perkin-Elmer 325 spectrometer was used and the maximum slit width used corresponded to a resolution of 3 cm^{-1}.

Upon heating the sample *in vacuo* to a measured temperature T(K) desorption takes place, causing a decrease in absorbance. Since for any adsorbed complex the absorbance A_x can be assumed proportional to the partial coverage θ_x the first order rate constant k_x defined by

$$\frac{-d\theta_x}{dt} = k_x\theta_x$$

is equal to

$$k_x = \frac{1}{A_x}\left(-\frac{dA_x}{dt}\right)\ (\mathrm{sec}^{-1}),$$

where k and h are Boltzmann's and Planck's constants, respectively. The free energy of activation $\Delta G^{\ddagger}$ for the desorption of this complex is then calculated from the value k_x measured by spectrokinetics and the temperature T.

X-Ray Diffraction Analysis

The alloy formation was examined by X-ray diffraction. Sintered MgO was used as an internal reference. Peaks for the Pd–Ag alloy (111), (200) and MgO (200) reflections were recorded at an angular speed of ¼° (2θ)/min. The crystal size of the alloy was determined by X-ray line broadening and electron microscopy.

RESULTS

All the supported alloy catalysts showed in X-ray diffraction diagrams a large alloy peak and a small peak of separated silver crystals. With increasing silver content of the samples, the intensity of the latter peak increased while the alloy peaks were broadened. Usually the Ag peaks were sharper indicating a larger size for the Ag particles than for the alloy particles. From the peak positions of the (111) and (200) lines of the alloy, the lattice constants were calculated. They are plotted in Fig. 1 against the composition calculated from the silver and palladium content of the sample, correcting for the unalloyed silver, the amount of which was determined from the line intensity. As the specific intensities of Pd and Ag diffraction lines are known to be almost equal, the relative quantities of Ag and the alloy were considered to be proportional to the corresponding (111) peak areas. With this correction the lattice constants showed good agreement with those of bulk alloys except in the $Pd_{90}Ag_{10}$ and $Pd_{39}Ag_{61}$ alloys. This is shown in Fig. 1, where the lattice

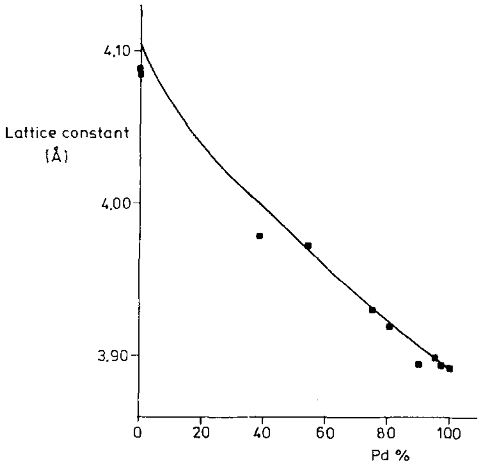

FIG. 1. Lattice constants for SiO_2-supported Pd-Ag alloys: (—) bulk Pd-Ag allloys [from Ref. (*14*)].

parameter of bulk alloys is shown by the drawn line (*14*).

The X-ray lines are broadened by two causes: (a) small crystal sizes and (b) differences in the actual composition of the individual alloy particles which lead to a distribution of the lattice constant around its average value. The apparent crystal sizes as determined from line broadening ignoring cause (b) were smaller for the Ag-rich alloys but significantly deviated from the sizes as determined by electron microscopy. It follows that for the Ag-rich samples the composition of the individual particles scattered by almost 100% around the average composition. These physical characteristics of alloy catalysts are shown in Table 1.

Infrared Spectra of CO Adsorbed on Pd

The method of preparation of the Pd/SiO_2 catalysts had only a small influence on the CO spectra; only the sample prepared from $Pd(NH_3)_4(NO_3)_2$ showed a spectrum somewhat different, as shown in Fig. 2. Since in this sample atomically dispersed Pd could be expected (*20*), it seems appropriate to say that here the "particle size effect" changed the spectra.

In addition to the three absorption bands (A, B, C bands) present on the alloys, two other bands were observed on Pd. A_0 at about 1840 cm^{-1} and E at 2085 cm^{-1}. These absorptions correspond to those of CO on nickel, although the relative intensities are somewhat different from those on nickel (*11, 15*). The identification of CO bands (A, A_0, B, C, E) was made according to the assignment of Yates and Garland on nickel (*15*).

The intensity of the B band changed with particle size and almost disappeared in a small particle sample such as P_{18}. As the CO coverage was slowly increased the A_0 and A bands appeared first while the B and E bands appeared at higher pressure than other bands. At high CO coverage the intensities of the A and A_0 bands decreased slightly and increased at an early stage of the evacuation. Reversible

TABLE 1
COMPOSITION AND PARTICLE SIZE OF Pd-Ag ALLOYS

Sample no.	Metal[a] (%)	Ag crystals (%)	Apparent particle size[b] by X-rays (Å)	Particle size by electron microscopy (Å)
9.75/2.5	$Pd_{97}Ag_{2.5}$	5.58	146	145
9.5/0.5	$Pd_{96.5}Ag_{3.5}$	0.92	160	
9/1	$Pd_{90}Ag_{10}$	1.85	180	199
8/2	$Pd_{81}Ag_{19}$	0.44	130	
7/3	$Pd_{75}Ag_{25}$	7.54	95	160
5/5	$Pd_{54}Ag_{46}$	9.24	80	106
3.5/6.5	$Pd_{39}Ag_{61}$	9.68	75	

[a] Metal % in alloys was corrected value, subtracting the amount of Ag crystals.
[b] Observed line width was considered to be caused from particle size only.

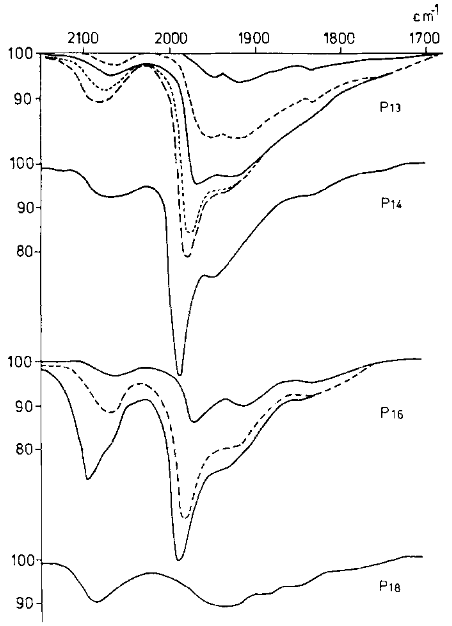

FIG. 2. Spectra of CO adsorbed on Pd/SiO$_2$ prepared by various methods: P_{13}, P_{CO} = 0.0002–0.1 Torr; P_{14}, 0.5 Torr; P_{16}, 0.0002–1.3 Torr; P_{18}, 0.89 Torr.

frequency shifts to higher frequencies by increasing CO coverage and shifts to lower frequencies upon evacuation were observed.

Infrared Spectra of CO Adsorbed on Pd–Ag Alloys

Small quantities of CO gas were adsorbed in a stepwise fashion on alloy catalysts and infrared spectra and the adsorbed amount were recorded. As for Pd the lower frequency bands ($<$2000 cm^{-1}) predominated in the spectrum and it was of interest to compare their absorbance with the amount of adsorbed CO determined volumetrically. The result in Fig. 3 shows a straight line passing through the origin up to a coverage of 70%. From this we conclude that virtually all chemisorbed CO is detectable in the infrared, i.e., dissociative adsorption is not significant at low coverage. On the alloys the absorbance does not fit the same line because in these cases the major band is the C band, which has an extinction coefficient different from that of the lower frequency bands which prevail for CO on Pd.

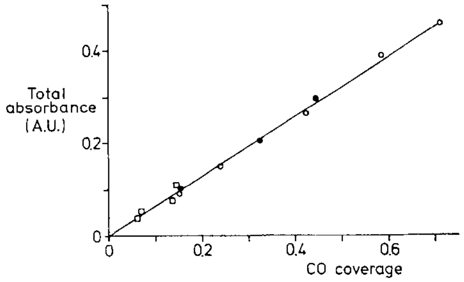

FIG. 3. Total absorbance of CO adsorbed on Pd as a function of CO coverage.

Figure 4 shows the infrared spectra of CO adsorbed on Pd and Pd–Ag alloys at room temperature. The CO pressure was 0.01 and 0.5 Torr, respectively. The Pd content in alloys was in the range of 97.5 and 38.9%. No absorption band was observed for the Ag/SiO$_2$ catalyst at this CO pressure. Three main CO adsorption bands, the A, B and C bands, were observed on alloys. It is remarkable that the bands A, B and C have virtually the same position for Pd and all alloys, but that their relative intensities differ greatly. The intensity of the two lower frequency bands (A, B) decreases with increasing Ag content in alloys as shown in Figs. 4 and 5. The ratio of the absorbance of the high frequency bands (C and E) as a function of total absorbance remained rather constant for Ag-rich alloys.

As each band might be due to adsorption complexes with different strengths of the adsorption band between CO and the metal, it is interesting to see whether the bands are formed in the order of decreasing heat of adsorption upon slowly admitting the gas. As CO was introduced in small doses the bands appeared in the order A $>$ C$>$ B $>$ E. The A and C bands attained their maximum intensity at a CO pressure of 0.01 Torr, but the B band on alloys or Pd and the E band on Pd continued to increase in intensity as the pressure was raised above 0.01 Torr. Shifts to higher frequencies with increasing CO coverage were observed especially on Pd and Pd-rich alloys. The frequency shift with coverage was reversible, i.e., the bands shifted toward lower frequencies

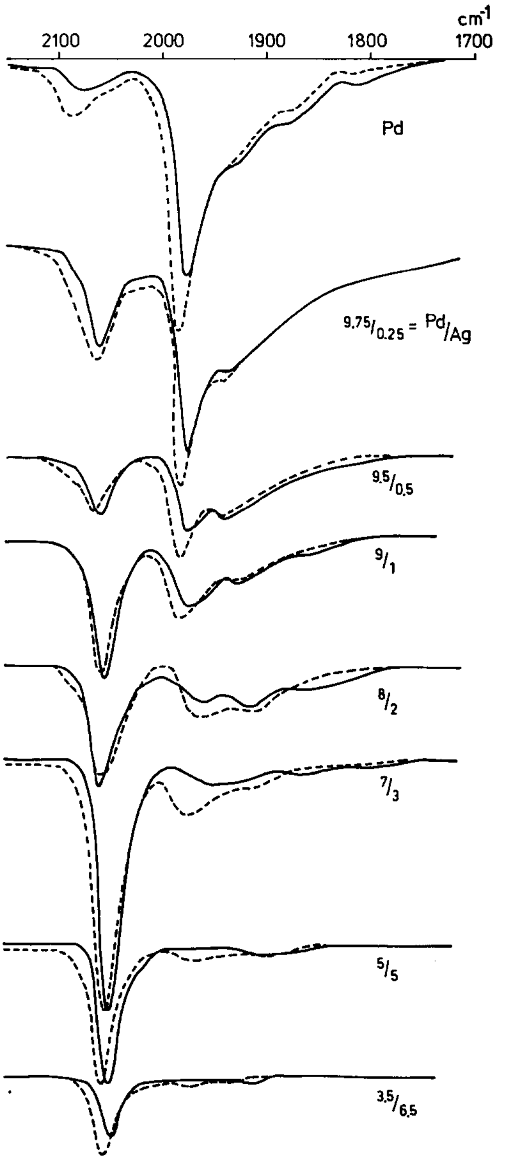

FIG. 4. Spectra of CO adsorbed on Pd–Ag alloys: (—) $P_{CO} = 0.01$ Torr; (- - -) $P_{CO} = 0.5$ Torr.

upon evacuation. No large frequency shifts with alloy composition were observed, as shown in Table 2, and Fig. 4.

The free energy of activation for desorption $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ is determined from the spectrokinetic desorption data as described in the experimental part. A complication arises by the fact that in our case some bands partially overlap. The resulting error, however, is small so that rough estimates of the free energy of activation for desorption can be given. Upon further evaluating these data one can, for instance, assume $\Delta S^{\ddagger} = 0$ in which case the free energy of activation coincides with the enthalpy of activation $\Delta H^{\ddagger}$. Further, since the activation energy of adsorption is very small in this case, one can consider the enthalpy of activation for desorption as numerically equal to the heat of adsorption $-\Delta H_{ads}$.

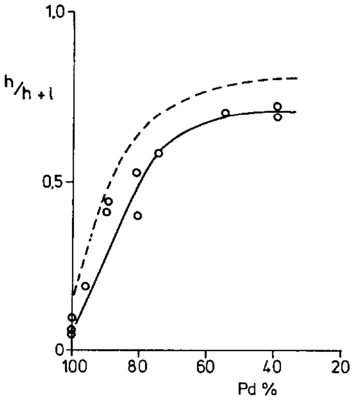

FIG. 5. Absorbance ratio of high frequency bands above 2000 cm⁻¹ to total absorbance of adsorbed CO as a function of Pd composition in Pd–Ag alloys: (○—) $P_{CO} = 0.01$ Torr; (- - -) maximum value of $h/(h+1)$.

Since in the present work we are interested in the change of $-\Delta H_{ads}$ upon alloying, it is not very important whether each of the above assumptions is exactly true. For instance, a finite value of $\Delta S^{\ddagger} \neq 0$ would not essentially influence the conclusions, provided that $\Delta S^{\ddagger}$ does not change much with alloy composition. The result is shown in Fig. 6 where the average activation energy corresponds to that due to desorbed CO which is about half the amount of CO adsorbed at 0.5 Torr. As shown in Fig. 6, the average activation energy of desorption changes little with alloy composition (31 kcal/mole on pure Pd to 27 kcal/mole on $Pd_{39}Ag_{31}$). The individual activation energies of desorption were determined for Pd, measuring desorption at 100°C for the B band and at 260°C for the A band. The estimated

TABLE 2

INFRARED ABSORPTION FREQUENCIES FOR CO ADSORBED ON Pd AND Pd-Ag ALLOYS[a]

Sample no.	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
Pd	2095 → 2060	1990 → 1960	1940 → 1910	1880 → 1865	~1815
9.75/0.25	2060 → 2047	1980 → 1962	1940 → 1915		
9.5/0.5	2060 → 2047	1982 → 1960	1940 → 1915		
9/1	2060 → 2047	1980 → 1960	1940 → 1910		
8/2	2060 → 2047	1975 → 1950	1935 → 1905		
7/3	2060 → 2045	1975 → 1950	1928 → 1900		
5/5	2060 → 2045	1980 → 1942	1930 → 1900		
3.5/6.5	2055 → 2045	1972	1925 → 1920		

[a] High CO coverage → low coverage.

activation energies were found to be 26 kcal/mole for the B band complex and 41 kcal/mole for the A band complex.

Spectra of CO Adsorbed on Palladium Hydride

To investigate the possible influence of the electronic factor for CO adsorption on Pd or Pd–Ag alloys from another angle, the spectra of CO adsorbed on Pd hydride or Pd–Ag hydride were measured. The magnetic properties of Pd saturated with hydrogen resemble those of Pd–Ag alloys. The magnetic susceptibility is known to decrease linearly with increasing hydrogen content in Pd, and when the content of (H)/Pd ~ 0.6 diamagnetism is observed [for Pd–Ag alloys less than 40% Pd (*16*)]. A transition from paramagnetism to diamagnetism upon hydrogen saturation also occurs in Pd–Ag-rich alloys.

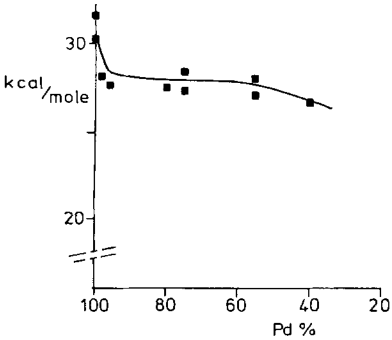

FIG. 6. Activation energy for desorption of CO on Pd–Ag alloys.

A pressure of 1 atm of hydrogen was applied to Pd or Pd-rich alloys until an equilibrium was established at room temperature where the ratio (H)/Pd was expected to be above 0.5. A small amount of CO was introduced (the amount of hydrogen in the gas phase was 300 to 500 times that of CO) and was allowed to diffuse in the hydrogen atmosphere. Three hours later the equilibrium of CO adsorption on the hydride was reached and the spectra were recorded. They are shown in Fig. 7 for Pd and $Pd_{97}Ag_3$ alloys and compared with the CO spectrum without hydrogen. No significant difference was observed in the CO spectra of the hydride compared with the hydrogen-free samples, except for small shifts to lower frequencies.

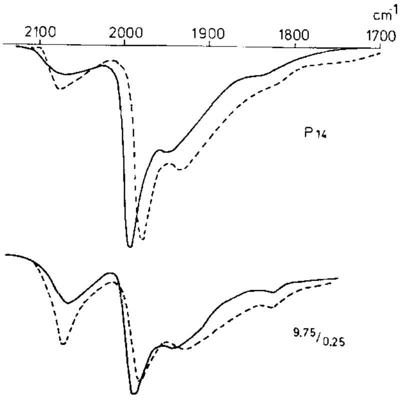

FIG. 7. Comparison of the CO spectra on Pd hydride, $Pd_{97.5}Ag_{2.5}$ alloy hydride (- - -) and those without hydrogen (—).

DISCUSSION

Alloying silver with palladium gives rise to a very pronounced change in relative band intensities but the band frequencies remain virtually unchanged (see Fig. 4 and Table 2). In our opinion, this is the most important result of the present work. It provides direct evidence of the relative importance of the two fundamental phenomena responsible for the peculiar catalytic properties of alloys, the "ensemble effect" and the "ligand effect," which were defined in the Introduction. For the system studied in this work the infrared spectra show that the ensemble effect is very marked but the ligand effect is of minor importance. To our knowledge this is the first experimental evidence proving the reality of the ensemble effect in an alloy catalyst.

For these conclusions the assignment of the bands is essential, and this assignment, which has been a controversial subject, can indeed be justified by the present results. As was indicated in the Introduction, the opposing assignment of the bands below 2000 cm^{-1} by Eischens (*10*) and by Blyholder (*12*) lead to different predictions for the CO spectra on Pd–Ag alloys. If Eischens' assignment is correct, one would expect that with increasing dilution of Pd with Ag the concentration of the bridge complex requiring a pair of adjacent Pd atoms would decrease more rapidly than the concentration of the linear complex. If, however, the electronic configuration of the adsorbed atom is the sole reason for the large frequency shift of the band, alloying of Pd with Ag would be expected to cause a marked and successively increasing shift in band position with increasing Ag content in alloys.

The experimental results clearly support Eischens' assignment, i.e., the C band at 2060 cm^{-1} is due to a linear bonding with Pd and the A$_0$, A and B bands are due to a bridged bonding. A similar result was found by Hobert (*17*) for the infrared spectra of CO adsorbed on Cu–Ni alloys. He likewise found a considerable decrease of the lower frequency band with alloying while the frequency shifts were rather small. The close resemblance of the Pd–Ag and Cu–Ni systems which show similar sensitivities in their CO spectra could not be predicted on the basis of the present electronic theory of alloys which shows that alloying with Ag fills the holes of the Pd *d*-state in Pd–Ag alloys (*18*) but that the population of the *d*-electrons in Ni is hardly influenced by Cu in Cu–Ni alloys (*19*).

The infrared spectra of CO adsorbed on Pd reported in the literature show some dependence on the preparation conditions used by different workers (*11–22*). These differences are ascribed to the different particle sizes and the different degrees of crystal imperfection. Our Pd catalysts had been reduced twice at rather high temperature resulting in quite reproducible spectra as shown in Fig. 2. If we follow the view expressed by Baddour, Modell and Goldsmith (*21*), our samples are in the stabilized or "break-in" form due to considerable rearrangement of the Pd atoms. All absorption bands of CO chemisorbed on Pd appear to have corresponding bands on Ni, although the relative intensities of the bands are different. Following Yates and Garland's (*15*) assignment for CO on Ni, the absorption bands on Pd may be classified in the same five groups:

A$_0$(1900–1800 cm^{-1}),
A$_1$(1950–1910),
B(1900–1950),
C(2075–2040),
E(2095–2075),

where the C and E bands are due to the linear bonding CO and the A$_0$, A$_1$, B bands due to the bridge bonding CO to Pd. The assignment by Garland for the CO bands on Ni hence also fits those on Pd. Furthermore we assume that the B band frequency which is rather high for an ordinary bridge complex is due to a bridge complex surrounded by other bridge complexes. The reasoning is as follows:

i. The B band appears only at high CO pressure and the desorption energy, 26 kcal/mole, is small compared with that of A or A_0 bands.

ii. The B band is not observed in samples with very small particles such as a P_{18} sample.

iii. Upon desorption of CO corresponding to the B band the intensities of the A and A_0 bands increased.

In addition to the position of the infrared bands further information about the electronic ligand effect of alloying on chemisorption is obtained from the desorption energy. Its average value changes very little with alloy composition. Since this average is mainly due to the bridged complex for Pd and for the linear complex for the Ag-rich alloys it would be desirable to know how the bond strength of each individual band changes with alloying. Unfortunately, such a detailed analysis is not possible because of the strong band overlap. The main band on alloys containing less than 70% Pd is the C band. The desorption energy on these alloys of about 27 kcal/mole, therefore, is mainly due to the linear CO complex. For Pd we find 41 kcal/mole for the bridged complex (the A band). The linear bonding on Pd is less stable than the bridge bonding and presumably equal to the linear bonding on the alloys. The energy of adsorption depends not only on alloying but also on the degree of coverage. For CO on Pd Christmann and Ertl (*9*) have observed that the energy of adsorption remains constant up to half coverage, but for CO on Pd–Ag alloys they found that the adsorption energy decreases continuously with coverage. This result can be understood qualitatively on the basis of the present findings. Since the bridged complex is much stronger than the linear complex, the present results show that for pure Pd, adsorbing CO molecules can form bridge complexes up to a very high coverage, whereas on Pd–Ag alloys ensembles for which a bridged complex is possible are exhausted at rather low relative coverages. Upon further adsorbing CO on these alloys only the weaker linear complex can be formed with a consequent decrease in the heat of adsorption. Whereas, the relative amounts of the bridged and the linear complexes depend on the alloy composition because of the geometric ensemble effect, the adsorption properties of the individual Pd atoms appear to change only little with alloy composition.

In addition to these facts the finding that CO spectra on Pd hydride did not show a marked change when compared with those on Pd appears to indicate that the effect of the electronic ligand factor on CO adsorption is rather small. $Pd_{30}Ag_{70}$ alloy and Pd hydride (β-phase) are both diamagnetic indicating that the Pd *d*-orbitals are filled. But the CO spectra are quite different as is shown in Figs. 4 and 7. Though the absorption bands on Pd hydride showed a small shift to lower frequencies as might be explained by electron back donation from the metal the shift is very small compared with the frequency difference of the C and the A (or B), bands. Similar studies of the role of an electronic factor on CO adsorption on transition metals have been made by Blyholder and Sheets (*23*) and by Queau and Poilblanc (*24*). Upon adsorbing CO on surfaces precovered with bases such as $(CH_3)_3N$, NH_3 or $C_2H_5N \equiv C$ the authors found that the CO band was only little affected by these electron donors. The constancy of CO band frequencies with alloy composition, the small effect of alloying on the heat of adsorption, the lack of any change in the spectra due to preadsorbed hydrogen and the comparison with the results on Ni–Cu alloys all consistently show that the ligand effect is relatively unimportant in this system. This result proves that a surface titration of these alloys by selective chemisorption with CO is, in principle, justified. However, the occurrence of the linear and the bridged complexes whose relative abundances change with alloy composition and degree of coverage are complications which must be taken into account when the number of Pd atoms in alloy surfaces is to be counted by means of chemisorptive titration. As a result of the predominance of the CO bridged complex on Pd metal, Brennan and Hayes (*25*) found a ratio adsorbed

CO molecules to surface Pd atoms of $\mathrm{CO/Pd} = 0.6$. On Ag-rich alloys most of the CO molecules are linearly adsorbed; consequently $0.6 < \mathrm{CO/Pd} < 1$.

In conclusion the statement can be made that information obtained by infrared spectroscopy of adsorbates on alloys is relevant to two problem areas:

i. Certain controversial problems with regard to the assignment of infrared bands of adsorption complexes on metals can be solved.

ii. Fundamental problems of the catalysis by alloys are treated by identifying the effects of alloying upon chemisorption.

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