JOURNAL OF CATALYSIS 59, 201–210 (1979)

Ligand and Ensemble Effects in the Adsorption of Carbon Monoxide on Supported Palladium–Gold Alloys

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Received March 15, 1978; revised February 20, 1979

The adsorption of carbon monoxide on a series of small particle palladium–gold alloys was investigated by infrared spectroscopy. Adsorbed carbon monoxide was detected on both the gold and palladium components of the alloy, and the positions, shapes, and intensities of the infrared bands were correlated with surface coverage and composition. The results of this study indicate that both ligand and ensemble effects are important when carbon monoxide is adsorbed on small, palladium–gold particles.

INTRODUCTION

Alloys between metals of Groups VIII and Ib have played an important role in catalysis. With the recent demise of the rigid band theory of transition metals as a result of photoelectron spectroscopy (*1*), emphasis has shifted from an electronic effect to a structural or dilution or ensemble effect which explains differences in surface reactivity with alloying by the change in surface concentration of groups of adjacent metal atoms of a given kind. Such ensembles are believed to be essential to the binding of certain molecules or to certain binding modes of a given molecule such as carbon monoxide. For instance the latter could be bound to a single atom in a linear form or to two adjacent atoms in a bridging mode as observed in metal carbonyls.

Nevertheless, electronic effects remain a possibility. In keeping with the new physical evidence suggesting the preservation of electronic structure of individual alloy components, the term ligand effect has been introduced (*2*) to denote the change in binding energy of a surface atom A when it is surrounded in part or totally by B atoms instead of A atoms exclusively. Evidence for both ligand and ensemble effects was provided in a study in thermal desorption spectroscopy of H_2 and CO adsorption on copper–nickel single crystal alloys (*3*).

Other studies by infrared spectroscopy of carbon monoxide adsorption on copper–nickel (*4*) and palladium–silver alloys (*5*) reveal shifts with alloy composition of both the position and intensity of the infrared bands. These were attributed to the influence of both "ligand" and "structural" effects in the alloy particles. These ir studies were carried out with relatively

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0021-9517/79/110201-10$02.00/0

large metal particles (~15 nm) or with systems such as Cu–Ni with surface enrichment in one component of the alloy (*6*). The current investigation was undertaken to examine the surface properties of small palladium–gold particles (~2 nm), a binary alloy which at least with small particles exhibits surface compositions similar to bulk compositions (*7*). The results of a study by ir absorption spectroscopy of CO adsorption on supported Pd, Au, and their alloys are reported in this paper.

EXPERIMENTAL

All samples used in this study were prepared by ion exchange onto Davison 950 Silica Gel as described previously for Au (*7*), Pt (*8*), and Pd complexes (*9*). Details of preparation and characterization are given elsewhere (*7*).

Merck, Sharpe and Dohme, Ltd. supplied ^{13}CO (94% ^{13}C) which was used as received. Hydrogen was purified by passage through a Pd thimble and was dried with molecular sieve at 77 K. Helium and carbon monoxide were dried by passage through molecular sieve traps cooled to 77 and 195 K, respectively.

Hydrogen and carbon monoxide chemisorption were measured on a volumetric system with a Texas Instruments precision pressure gauge (*10*).

Infrared measurements were made with a Beckman 1R7 with a resolution of 5 cm^{-1}. The infrared cell followed a design of Yates (*11*) and was connected to a vacuum system with a MKS Baratron capacitance pressure gauge (*12*).

The samples used for infrared study were ground in an agate mortar to a fine powder and were compressed into thin wafers under 1×10^4 lb/in.^{2} pressure. The "thickness" of the samples used in the infrared spectrometer was 14 mg/cm^2. All of the Pd–Au samples were reduced at 573 K with flowing H_2 (30 cm^3/min) for 1 hr and evacuated for 1 hr at the same temperature prior to cooling to room temperature for ir measurements.

RESULTS

Carbon Monoxide Adsorption on Small Palladium Particles

In their pioneering studies, Eischens *et al.* reported two sets of ir bands of carbon monoxide adsorbed on supported palladium (*13, 14*). A symmetric band was observed at 2070 cm^{-1} while a broad band with several low-frequency shoulders had a maximum intensity at 1930 cm^{-1}. Subsequent studies of CO on supported Pd have reported spectra with the same general appearance but with bands at significantly different positions (*5, 15–18*). This variation in band position has been most evident below 2000 cm^{-1} where the maximum has been observed at frequencies as high as 1980 cm^{-1}. The position of the lower frequency band seems to be dependent upon the techniques used to prepare the sample, and the wide variations in position have been attributed to a particle size effect (*16*).

Since a particle size effect may influence the spectrum of CO adsorbed on Pd, the first step in investigating a series of small particles Pd–Au alloys must be the examination of the Pd component alone. The Pd samples used in this study had a dispersion of 60% corresponding to ca. 1.5-nm metallic particles, as determined by both carbon monoxide and hydrogen chemisorption according to Benson *et al.* (*19*).

The spectra of CO adsorbed on this highly dispersed Pd sample are shown in Fig. 1. Curves 1, 2, and 3 were recorded after small quantities of gas were admitted to a sample positioned in the beam of the spectrometer. The CO pressure in the system after each adsorption was too low to measure (0.00 Torr). One band centered at 1870 cm^{-1} dominated the spectrum at pressures less than 1×10^{-2} Torr. Curve 4 was recorded at a pressure of 0.02 Torr.

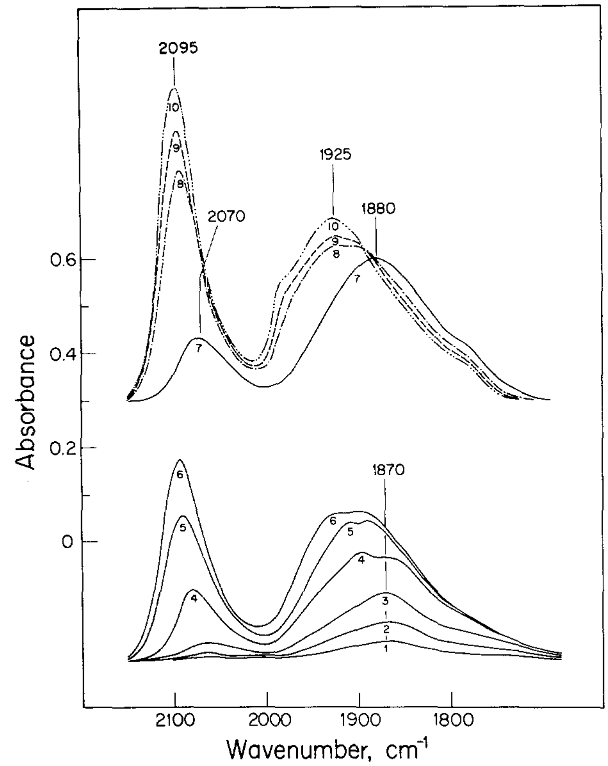

FIG. 1. Carbon monoxide adsorption on silica-supported palladium. Spectra (1–3), 0.00 Torr; (4) 0.02 Torr; (5) 0.85 Torr; (6) 7.48 Torr; (7) after evacuation for 1 hr, 1×10^{-5} Torr; (8) 7.50 Torr; (9) 50.0 Torr; (10) 300.1 Torr.

The increased pressure brought about significant changes in the spectrum. New bands appeared at 1900 and 2080 cm^{-1}. Further increases in pressure to 0.85 Torr (curve 5) and 7.48 Torr (curve 6) produced more intense bands that shifted toward higher frequencies.

When the gas phase CO was removed by evacuation, the bands shifted toward lower frequencies. Spectrum 7 was recorded with a pressure of less than 1×10^{-5} Torr after evacuation for 1 hr. No further changes in the spectrum were observed for longer periods of evacuation. The irreversibly bound CO had bands at 2070 and 1880 cm^{-1}. The position of the lower frequency band was very similar to the position of the band maxima of spectra 1, 2, and 3 that were recorded after the first small quantities of CO had been added to the sample.

After the evacuation step, CO at 7.50 Torr (1.00 kPa) was readmitted to the palladium sample and curve 8 was recorded. This was almost identical to spectrum 6. Cycles of evacuation and readmission of CO at 7.50 Torr consistently reproduced spectra 7 and 8.

The addition of gaseous CO to the sample after evacuation brought about a very significant change in the spectrum. The entire lower frequency band appeared to shift to higher frequencies. This phenomenon did not occur with the band above 2000 cm^{-1}. Further shifts in the lower frequency bands occurred in spectrum 9 at 50.0 Torr and in spectrum 10 at 300.1 Torr. At a pressure of 300 Torr the lower frequency band had a maximum at 1925 cm^{-1} and at a distinct shoulder at 1980 cm^{-1}.

Each group of bands was asymmetric

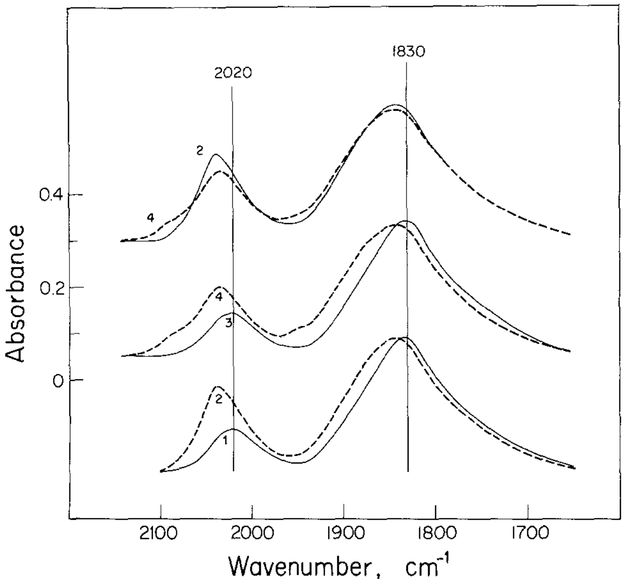

FIG. 2. Sequential adsorption of ^{13}CO and ^{12}CO on supported palladium. Spectrum (1) after exposure to 7.50 Torr of ^{13}CO and subsequent evacuation for 1 hr; (2) addition of 0.04 Torr of ^{13}CO; (3) after evacuation for 1 hr; (4) addition of 0.04 Torr of ^{12}CO.

on the lower frequency side and each showed a changing maximum as the CO pressure was increased. When spectrum 7 of the irreversibly adsorbed CO was subtracted from spectrum 8, a symmetric band resulted at 2100 cm^{-1}. This difference spectrum of the reversible adsorption is shown in Fig. 5. The same result occurred for curves 9 and 10. Subtraction of the spectrum recorded after the evacuation step from subsequent spectra produced a symmetric band centered at 2100 cm^{-1}. This has been found to be true over the pressure range of 0.1 to 300 Torr. This result is highly suggestive that the band above 2000 cm^{-1} was the superposition of two noninteracting bands, one produced by a reversibly adsorbed form of CO and the other produced by an irreversibly bound form.

The technique of substracting one spectrum from another to observe the net effect of increasing adsorption cannot be applied to the lower frequency bands because of significant shifts that would result in negative intensities at some positions in the spectrum. This result alone shows that the lower frequency bands are not produced by CO molecules adsorbed on a discrete set of noninteracting sites. Instead it indicates that the molecules producing the spectrum were influenced by adsorbate–adsorbate interactions. The effect of intermolecular interactions on the positions of the bands has been confirmed by using isotopically labeled carbon monoxide.

The results of an experiment using isotopically labeled molecules are shown in Fig. 2. Curve 1 is the spectrum of irreversibly adsorbed ^{13}CO that was recorded after initially equilibrating the palladium sample with 7.50 Torr of ^{13}CO and then removing the gas phase and weakly adsorbed molecules by evacuating for 1 hr. The positions of both bands shifted by approximately 50 cm^{-1} from those observed with ^{12}CO. Spectrum 2 was recorded after admitting 0.78 μmol of ^{13}CO to the sample. The pressure in the system was 0.04 Torr. The addition of a small quantity of CO caused the lower frequency band to shift its position with no significant change in intensity.

Spectrum 3 was recorded after a second evacuation period of 1 hr and reproduced curve 1. The result of adding 0.78 μmol of ^{12}CO to the irreversibly adsorbed ^{13}CO is shown in spectrum 4. A small quantity of ^{12}CO caused the lower frequency band to shift toward higher frequencies and the 2040 cm^{-1} band to increase in intensity, a result similar to that produced by an increment of ^{13}CO. The coincidence of these results is emphasized at the top of Fig. 2 where spectra 2 and 4 are superimposed. The addition of ^{12}CO instead of ^{13}CO produced the same shift in the low frequency band.

The results of adding ^{12}CO to preadsorbed ^{13}CO demonstrate that the changes in the lower frequency band are produced by the interaction of irreversibly adsorbed ^{13}CO with the reversibly bound ^{12}CO. If the shift in the spectrum had been caused by adsorption on additional sites, the increment of ^{12}CO should have produced an intense band at 1900 cm^{-1}. It did not. Instead the lower frequency portion of the spectrum was found to be the same whether ^{12}CO or ^{13}CO was added to the preadsorbed carbon monoxide. This indicates that the band is produced by the ^{13}CO initially on the surface and that the shifts in position of the lower frequency band are brought about by interactions between the irreversibly adsorbed ^{13}CO and the pressure dependent form of adsorption.

The ir spectra reveal only two forms of irreversibly adsorbed CO on small Pd particles. The adsorbed form producing the band below 2000 cm^{-1} is very sensitive to interactions with other adsorbed molecules. The adsorbate–adsorbate interactions are responsible for the structure of the low-frequency band. This structure does not indicate several adsorbed forms, but differing local environments for the same form of adsorbed CO. By contrast, the irreversible adsorption that produces the band at 2070 cm^{-1} is not sensitive to perturbations by other adsorbed CO molecules.

Carbon Monoxide Adsorption on Small Particle Palladium–Gold Alloys

The preliminary investigation of CO adsorbed on small palladium particles showed that there were two forms of irreversible adsorption and one form of pressure-dependent adsorption. In order to examine the behavior of all three surface species on Au particles and a series of Pd–Au alloy particles of comparable size (1.5 to 4.5 nm) two standard conditions of investigation were chosen. The spectrum of each sample was examined at a CO pressure of 7.50 Torr to characterize the alloy surface when both reversible and irreversible forms of adsorption were present. Subsequently, CO in the gas phase and weakly bound CO were removed by evacuation for 1 hr, and then a second spectrum was recorded. This second spectrum provided information on the irreversibly adsorbed forms of CO. The difference between these two spectra revealed the bands associated with the reversible adsorption alone.

The conditions that provided interesting spectra of CO adsorbed on Pd also showed the spectra of CO adsorbed on gold. Yates has demonstrated that carbon monoxide is reversibly adsorbed on reduced Au particles and produces a band at 2115 cm^{-1} (*11*). This band at 2115 cm^{-1} revealed the presence of Au on the alloy surfaces.

Figures 3 and 4 show the spectra obtained for a series of small particle Pd–Au alloys at 7.50 Torr and after the evacuation procedure. Nominal Pd concentrations in the alloys are listed on the figures, but detailed compositions are provided in Table 1.

Variations in alloy composition affected both the positions and intensities of the CO spectra. Figure 3 shows the spectra of adsorbed CO when the pressure was 7.50

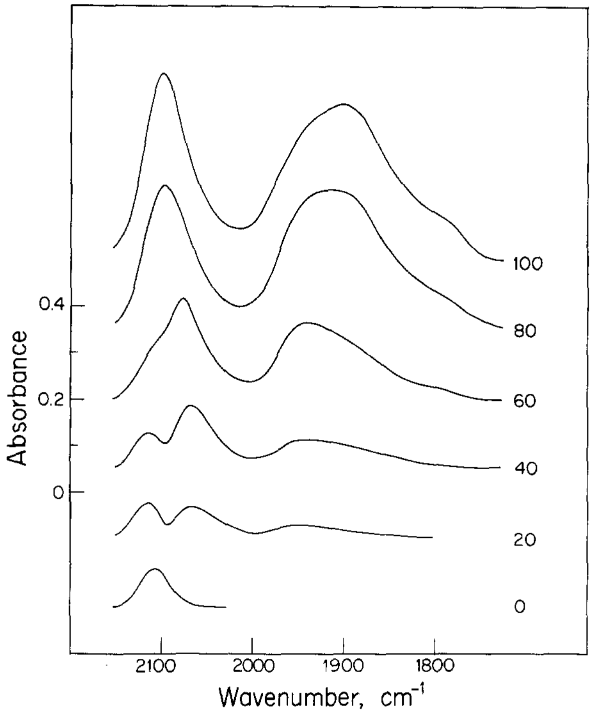

FIG. 3. Spectra of carbon monoxide adsorbed on series of palladium–gold alloys: P_{CO} = 7.50 Torr.

Torr. The band maxima of the pure Pd sample were at 2095 and 1900 cm^{-1}. As the Pd concentration was reduced, the position of the higher frequency band shifted toward lower frequencies. When the Pd concentration was reduced to 20%, the band initially located at 2095 had shifted to 2060 cm^{-1}, and a new band had appeared at 2115 cm^{-1} due to CO adsorption on Au.

TABLE 1

Composition of Palladium–Gold Samples

Pd (mol%)	Au (mol%)	Pd (μmol/g)	Au (μmol/g)	Irreversible CO chemisorption (μmol/g)
100	0	227	0	135
79.2	20.8	197	52	98
57.9	42.1	158	114	52
41.0	59.0	92	133	26
20.3	79.7	48	188	9
0	100	0	217	0

Reducing the Pd concentration in the alloy particles caused the band initially at 1900 cm^{-1} to shift toward higher frequencies. However, the preliminary experiments with Pd have shown that the position of this band is determined by intermolecular interactions rather than by changes in the chemical nature of the Pd surface. The spectra of irreversibly adsorbed CO presented in Fig. 4 showed similar trends. The band observed at 2070 cm^{-1} for pure Pd shifted to 2055 cm^{-1} when the Pd concentration was reduced to 20%. The spectra of reversible CO adsorption at 7.50 Torr are shown in Fig. 5. These spectra were obtained by taking the difference between the spectra presented in Figs. 3 and 4. The band located at 2100 cm^{-1} for pure Pd shifted to 2070 cm^{-1} when the Pd concentration was reduced to 20%. The band produced by CO adsorption on Au showed little variation as the alloy composition was changed.

The spectra presented in Figs. 3–5 show that changes in alloy composition affect both the position and intensity of the bands. In order to correlate the band intensity with population of surface molecules, volumetric adsorption measurements were made on separate samples of supported Pd, Pd–Au, and Au. The quantity of irreversible adsorption was determined from the difference between an initial isotherm and a second isotherm measured after a 1-hr evacuation period (Table 1).

The correlation between total integrated intensity of the bands produced by irreversible adsorption and volumetric measurements is shown in Fig. 6. The squares are data that were determined for the series of Pd–Au alloys using spectra presented in Fig. 4. The circles are data obtained from Fig. 1 for a pure Pd sample at varying degrees of surface coverage. All of the points in Fig. 6 fell along a straight line demonstrating that the intensity of the bands adequately represented population of irreversibly adsorbed CO.

The variation in band intensity of both types of irreversibly adsorbed CO is plotted in Fig. 7 as a function of total Pd concentration. The integrated intensity of the high-frequency band varies linearly with Pd concentration while the intensity of the low-frequency band changes quadratically.

Figure 5 shows the bands above 2000 cm^{-1} produced by reversibly adsorbed carbon monoxide at 7.50 Torr. The intensity of the band produced by adsorption on Pd also showed large changes as the alloy composition varied. But a quantitative measure of intensity cannot be made because of overlap with the band at 2115 cm^{-1} produced by CO adsorption on gold. Nevertheless the variation appears to follow the same concentration dependence as for the bands below 2000 cm^{-1}. This observation is consistent with the data presented in Figs. 1 and 2 which show that the low-frequency band interacts strongly with reversibly adsorbed CO.

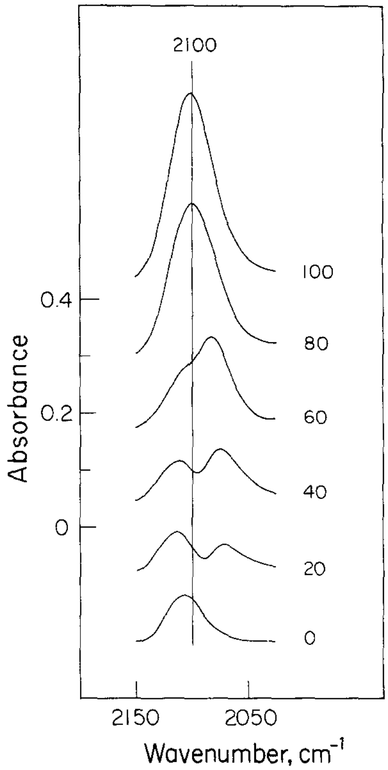

FIG. 4. Spectra of carbon monoxide adsorbed on palladium–gold alloys: irreversible adsorption.

DISCUSSION

Carbon Monoxide Adsorption on Small Palladium Particles

The influence of intermolecular interactions on the band position of adsorbed carbon monoxide has been reported recently for an annealed palladium film (*20, 21*). Hoffmann and Bradshaw have shown that an exposure of 3L of CO produced a band at 1930 cm^{-1}. When the exposure was increased, the band shifted toward higher frequencies until a maximum position was achieved at 1987 cm^{-1} under a constant pressure of 1×10^{-6} Torr. These results may be correlated with those of LEED experiments that show a continuous compression of the adsorbed CO

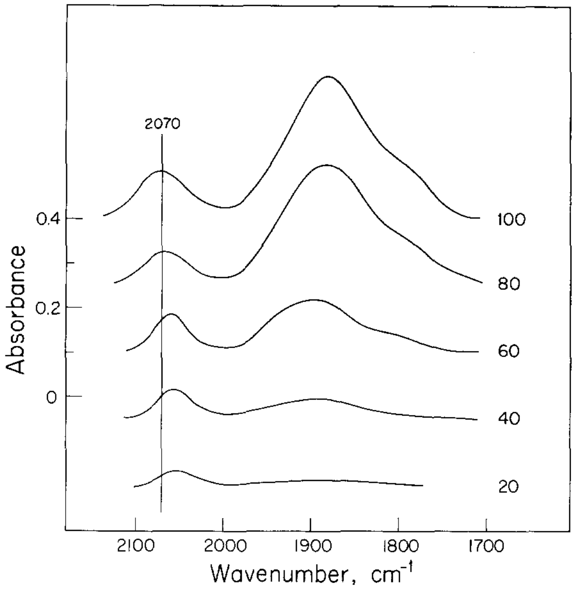

FIG. 5. Spectra of carbon monoxide adsorbed on palladium–gold alloys: reversible adsorption.

layer on low index faces of palladium single crystals (*22–27*). Hence it appears that decreasing CO intermolecular distances on the metal surface cause the band to shift until it stabilized at 1987 cm^{-1} when minimal intermolecular separation was achieved.

The work of Hoffmann and Bradshaw shows that when compressed layers of CO form on a Pd surface, a band appears at approximately 1990 cm^{-1}. Bands at similar position have been reported for supported Pd (*5*, *16*, *17*) films. In contrast, the 1.5-nm particles used for the present study displayed a band at 1880 cm^{-1}. Large difference in band position indicates that intermolecular interaction is much less pronounced on small particles at low pressures than on larger particles.

The band observed at 1880 cm^{-1} with our small Pd particles changes its position

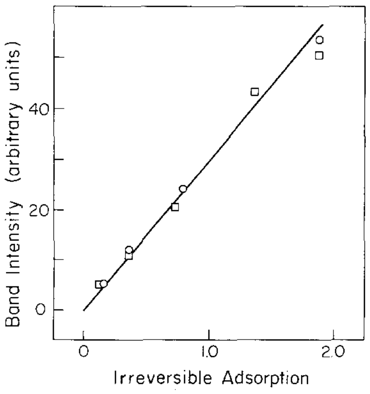

FIG. 6. Irreversible adsorption: dependence of band intensity on quantity of CO adsorbed: □ spectra in Fig. 4; ○ spectra in Fig. 1.

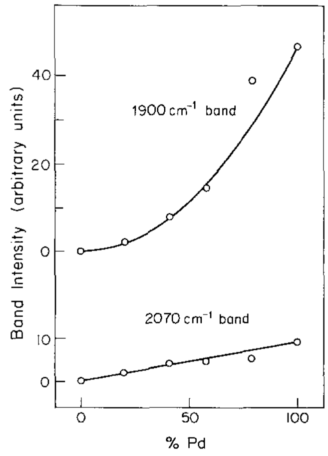

FIG. 7. Dependence of infrared band intensity in Fig. 4 on palladium content.

when a reversible form of CO is present. The use of isotopically substituted molecules showed that the shift in position is produced by interaction between the irreversibly adsorbed and the pressure-dependent forms. When the pressure was increased to 300 Torr, the band maximum had shifted to 1925 cm^{-1} and a shoulder had developed at 1980 cm^{-1}. The spectrum there resembles others observed for larger metal particles at both high and low pressures (*17*). This last observation supports the contention that interactions between irreversibly adsorbed molecules are stronger on large particles than on small particles. This may be due to the absence of compressed CO layers on small clusters, with a greater separation between adsorbed molecules than on larger particles with well-developed crystalline shapes.

Carbon Monoxide Adsorption on Small Particle Palladium–Gold Alloys

The infrared spectra of CO adsorbed on a series of supported palladium–gold alloys show changes in band position and intensity as the Pd content was reduced. Changes in position and intensity will be discussed in turn.

The dilution of Pd among Au atoms causes the position of the bands above 2000 cm^{-1} to decrease in frequency in response to the changing chemical environment around Pd atoms. These observations can be interpreted by a ligand effect since the positions of the high-frequency bands do not change with surface coverage. An increase in catalytic activity of Pd with Au dilution for the H_2–O_2 reaction on the same samples as used in this work was also recently interpreted by a ligand effect (*29*). By contrast, the bands near 1900 cm^{-1} show little variation in position with alloy composition. A decrease in frequency of these bands as reported by Primet *et al.* (*5*) for CO on Pd–Ag alloys with decreasing Pd content can be ascribed to decreasing adsorbate–adsorbate interactions on the large particles with increasing Pd dilution. On the smaller particles used in our work, these interactions appear to be less important on pure Pd as discussed above and therefore do not vary significantly with alloy composition.

On the other hand, the variation in band intensity with alloy composition appears to show an ensemble effect. For irreversibly adsorbed CO, the intensity of the low-frequency band depends almost quadratically on Pd concentration while the intensity of the high-frequency band depends linearly on Pd content. Very clearly, in a qualitative manner, if the high-frequency band corresponds to adsorption of CO on a single Pd atom site, then the low-frequency band corresponds to adsorption of CO on a site containing more than one Pd atom. To determine the size of the ensemble quantitatively would be a bit too speculative as it would rely on the assumption that surface and bulk compositions of the alloys are the same. While the latter appears to be a reasonable assumption (*7*), the qualitative existence of an ensemble effect is all that will be emphasized at the moment.

CONCLUSION

This study shows that the position of the bands of adsorbed carbon monoxide observed below 2000 cm^{-1} is affected by intermolecular interaction between the adsorbed species on palladium. This interaction appears to be more important on larger particles than on smaller particles, accounting for the difference in spectra observed for large and small metal particles.

The spectra of carbon monoxide adsorbed on a series of small particle, palladium–gold alloys can be interpreted by both ligand and ensemble effects. The ligand effect influences the position of the high-frequency bands. The ensemble effect influences the intensity of these same bands. The variation in band intensity supports qualitatively the original contention of Eischens *et al.* (*14*) that the low-frequency band is produced by carbon monoxide adsorbed on multiple palladium atoms sites while the other bands are produced by adsorption on individual palladium atoms.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation under the provisions for the US–USSR Exchange Program in Chemical Catalysis, Grant NSF CHE 18608.

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