JOURNAL OF CATALYSIS 36, 338–350 (1975)

The Infrared Spectrum of Carbon Monoxide on Reduced and Oxidized Palladium

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Received August 13, 1974

The spectra of carbon monoxide adsorbed on a silica-supported, 9% palladium catalyst has been studied in conjunction with adsorption studies of carbon monoxide and oxygen. Both bridged and linear species are observed. These species both react readily at room temperature with gas phase oxygen, and a pre-adsorbed oxygen layer reacts rapidly with gaseous carbon monoxide to yield the same spectrum as that on the reduced catalyst. If the catalyst is subjected to bulk oxidation, however, the spectrum of adsorbed carbon monoxide changes dramatically; the linear form is greatly enhanced and the bridged species becomes greatly reduced. No bands ascribable to adsorbed carbon dioxide are observed. Evidence is presented that some of the several separate bands seen for bridged species stem from the same species interacting to differing degrees with neighboring chemisorbed carbon monoxide. Estimates based on adsorbed amounts suggest that the bridged species has an extinction coefficient an order of magnitude greater than that for the firmly bound linear species but that a loosely bound linear species has an extinction coefficient more comparable to that of the bridged species. A model is suggested for the mode of adsorption that assumes both linear and bridged carbon monoxide bound to the same metal atom.

INTRODUCTION

Twenty years ago Eischens, Pliskin and Francis (*1*) reported that clear-cut infrared spectra could be obtained for chemisorbed carbon monoxide on silica-supported metal catalysts. In the classic series of papers following this initial report, Eischens and co-workers (*2–5*) showed that the observed bands could be divided into two main groups, those occurring above and below 2000 cm^{-1}. On the basis of analogies to transition metal carbonyls (*6*) the bands above 2000 cm^{-1} were assigned to linear species bound to a single surface atom and those below 2000 cm^{-1} were assigned to a bridged species bound to two surface atoms. For nickel and palladium catalysts both species were observed and it was further noted that the bridged species was the first to appear on adsorption and the last to disappear on desorption. Further scrutiny of the band due to their "bridged" species on palladium revealed that, at low coverages, the band center occurred at 1837 cm^{-1}. With successive doses the original band grew in intensity and new peaks appeared progressively at 1872 and 1925 cm^{-1}. In the spectra for the saturated surface a broad envelope with a peak at 1925 cm^{-1} was observed but shoulders, corresponding to the 1872 and 1837 cm^{-1} peaks (shifted to higher frequencies) were still observable. Although isotopic experiments for platinum had indicated (*2,5*) shifts due to interactions of neighboring linear molecules, Eischens *et al.* (*2*) interpreted the observations on nickel and palladium as follows: "The heterogeneity indicated by the spectra of CO on these metals is that in which the surface is divided into two or three major components which must be considered individually in the distribution

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of sites. Each component is subject to interaction effects. This behavior is similar to that expected from the exposure of more than one crystal face." Recently Soma-Noto and Sachtler (*35*) reported results from Pd and Pd-Ag alloys to support Eischens' assignment of CO bands on transition metals.

Since this paper first appeared, there have been criticisms of the original assignment to bridged and linear species. Blyholder (*7*), in particular, espouses the view that bridged species are not needed and that the various observed bands represent different linear species with varying degrees of back-bonding of d orbitals with π^* orbitals. This description is similar to one proposed by Cotton and Kraihanzel (*8*) for metal carbonyls. Despite this criticism, the fact remains that the spectrum of adsorbed carbon monoxide is rich in detail, and that these details, even for a given metal, are a sensitive function of the disposition of the metal component. Thus, the spectrum of adsorbed carbon monoxide has been utilized as a probe of the surface structure (*9*) in studies aimed at elucidating the effects of support, (*2*) metal particle size (*10–13*), the nature of alloy surfaces (*2,14*) and the nature of changes during catalytic reactions (*15,16*). The complexity of the spectra is often bewildering; for example (counting shoulders as well as peaks) as many as three bands assignable to bridged species and four bands assignable to linear species have been reported on nickel catalysts (*2*).

In this paper we report some detailed results obtained with a single batch of silica-supported palladium which suggest that the B species (*17*) is a single species and that the occurrence of peaks and shoulders at a variety of positions may stem from interactions of adsorbed species rather than a multiplicity of species on a multiplicity of sites. This interpretation is attractive insofar as it agrees with LEED experiments which suggest that, on exposure to low pressures of carbon monoxide, the 111, 100 and 110 planes all form bridged species between two palladium atoms 2.73 Å apart (*18*). It also is consistent with the observation that all planes are equally effective in the oxidation of carbon monoxide (*18*) and offers experimental support for a limiting theoretical description (*19*) wherein chemisorption can decouple metal orbitals to form a "surface molecule."

EXPERIMENTAL

The catalyst was prepared by impregnation of Cabosil (Grade M-5) with sufficient 5% $PdCl_2$ to yield a catalyst with a nominal 9% palladium. The powder was dried at 60°C and pressed (1t/cm^2) into self-supporting disks which were 20 mm in diameter and weighed about 100 mg. In the initial pretreatment the sample was reduced in a hydrogen stream for 10 hours at 300°C and then evacuated for a period of approximately 2 hours until the residual pressure was below 10^{-5} torr. Several samples were examined with reduction schedules different from the above, i.e., shorter times and/or higher (400°C) temperatures. The results for these several samples, however, were comparable to those reported herein; hence, the finer details of the reduction procedure were not significant in these experiments. Some changes in spectra were detectable even on a given sample as the catalyst aged, i.e., was exposed to various gases and reactivated. These changes, however, were relatively minor and involved primarily small changes in band intensities which could be ascribed to initial sintering of the metal particles. After several reactivations the reproducibility, even for band intensities, was excellent. In order to permit valid direct intercomparisons of the resulting spectra, the same aged sample was used in all the results reported herein.

The infrared cell is similar to the design described by Palazov (*20*) and permits positioning of the sample in the IR beam or transfer to an oven. The attached vacuum system had provisions for evacuation, circulation, and measured dosing of gases but, since the volume of the system was large (about 1000 cc) and the amounts of adsorption were small (about 0.20 cc STP), estimates of adsorbed amounts were made only for the irreversibly adsorbed gases.

Spectra were obtained on a Perkin-Elmer 521 grating instrument with an activated palladium-silica sample in the reference beams. Although the reference sample compensated for most of the silica absorption (strong bands at 1870 and 1640 cm^{-1}), the match was not perfect. Accordingly, all spectra shown in the figures have had the background prior to adsorption subtracted from the tracing. [Such a procedure is not free of danger. Perturbation of background bands by adsorbed gases or limited instrument response in regions of strong adsorption can cause uncertainties in these regions. Nevertheless, since these adsorbing gases interact directly with the metal and the reproducibility is very good, we view these dangers as minimal in the present study.] All spectra were obtained at room temperature.

The spectrum of adsorbed carbon monoxide was obtained by addition of a measured dose of gas, noting when the residual pressure stabilized, and then recording the spectrum. Unless otherwise noted, such spectra were stable insofar as no large changes with time were noted for periods up to 1 hour. In some cases a small amount of the residual gas was found to be condensable at −195°C. This gas, presumably CO_2, never amounted to more than about 1% of the capacity of the sample for CO. This small by-product of adsorption could have resulted from disproportionation or reaction with residual oxygen or water on the catalyst, but we have no firm evidence on this point. Since the amount was small and CO_2 produces no IR bands, we simply corrected the residual gas for this impurity and ignored it.

Samples were reactivated by oxidation, degassing, re-reduction by hydrogen at 300°C for 20–30 minutes and evacuation to remove adsorbed hydrogen. In some cases the catalysts were pretreated in oxygen. Such oxygen pretreatments were carried out at the indicated temperatures for 5–10 minutes at a pressure of 20 torr.

A number of adsorption experiments were carried out on a BET system with a 0.9 g sample of catalyst from the same batch as that used for the infrared experiments. This catalyst was pretreated by reduction at 400°C and evacuation for three hours at 400°C in order to carry out the particle size determination by the hydrogen adsorption procedure suggested by Aben (*21*). In order to match as closely as possible the conditions used in the infrared experiments, the sample for adsorption experiments was first pressed into disks similar to those used in IR studies and broken into large chunks.

RESULTS

Adsorption experiments. Adsorption experiments with a BET system were carried out on the larger sample to permit more quantitative statements than were possible in the IR studies. Hydrogen chemisorption measurements, following Aben's procedure (*21*), showed that 1.26 cc hydrogen adsorbed on 0.9 g catalyst. This value suggested 14.5% of the palladium atoms were on the surface and corresponded to a surface area of 69 m^2/g Pd with average palladium particle size of 70 A. After a series of adsorption measurements and intervening reactions, this value was reduced to 14%; hence, this seems to represent a stable value for the dispersion of this catalyst.

Isotherms for carbon monoxide were relatively flat. The amount of carbon monoxide adsorbed at 100 torr pressure was 2 cc/g. Evacuation for 15 minutes at room temperature and readsorption revealed that 10% of the carbon monoxide was removable by this procedure. The ratio of irreversible carbon monoxide chemisorption to the irreversible hydrogen chemisorption was 1.5, a value intermediate between the "standard" values suggested by other authors (*26,27*).

An isobar was run with both carbon monoxide and oxygen from below room temperature up to 300°C. Isobars for carbon monoxide were nearly flat from room temperature up to 200°C which suggests that (at 7 mm) the surface was nearly saturated. At higher temperatures there was some evidence of carbon dioxide evolution. This evolution, presumably due to the disproportionation:

$$2CO \rightarrow C + CO_2,$$

could be measured readily by circulation of the CO over the catalyst via a liquid nitrogen trap to trap the carbon dioxide which is readily removable from the catalyst and measuring the amount of trapped gas. At 300°C, such a measurement suggested that 0.18 cc of CO_2 formed in 1 hour at a pressure of 100 mm. This corresponds to a carbon laydown corresponding to 10% of the amount of irreversibly bound carbon monoxide. Below 200°C this reaction was undetectable under these conditions. Thus, this reaction is probably not important for any spectra reported herein, except for those recorded after degassing above 200°C. Since even in these runs (Figure 2) the temperature is below 300°C, where the reaction is known to be slow, the extent of the disproportionation reaction should be slight.

Figure 1 shows the isobar for oxygen adsorption at a pressure of 10 torr. On the right side the scale is expressed in terms of atom ratios of oxygen to palladium. If we assume that the uptake below 200°C represents mostly atomic chemisorption with one oxygen atom per surface palladium, we obtain similar dispersions (10 to 15%) to those obtained by hydrogen chemisorption measurements. Above 200°C, however, there is a dramatic increase in the oxygen uptake. Moreover, below 200°C there is little increase in adsorption after an hour, but above 200°C a slow, continuing sorption process is evident. (Points shown represent adsorptions recorded after about one hour even though the slow sorption process is still continuing.) These

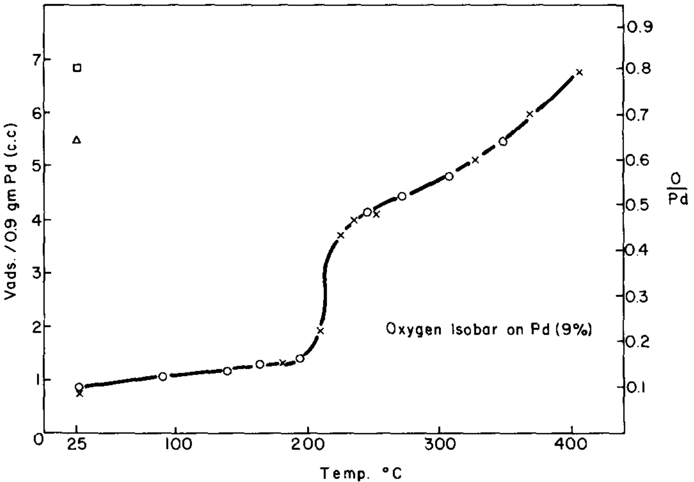


FIG. 1. Isobar for Oxygen (at 10 mm) on Palladium. Run 1: 0 Adsorption point, △ Desorption point. Run 2: X Adsorption point, □ Desorption point.

data clearly suggest that, at low temperatures, the uptake is primarily chemisorption on the surface of reduced palladium and that above 200°C the uptake is primarily bulk oxidation which becomes progressively more extensive as the temperature is increased. Desorption, as expected, does not occur when temperature is lowered back to 25°C.

Spectra of CO on reduced Pd. Figure 2 shows the spectra for adsorbed CO as successive doses were added to the reduced sample. For sufficiently small doses the bridged form (B_1) was evident at about 1900 cm^{-1}. The spectrum (a) after addition of the first dose (0.5 cc/g) shows two separate bands with maxima at 1970 (B_2) and 2070 (L_1) cm^{-1}, respectively. In this spectrum the lower frequency band shows a shoulder at about 1900 cm^{-1}. Since successive doses were completely adsorbed until the cumulative amount adsorbed was 1.7 cc/g, this initial dose corresponds to a 30% coverage with irreversibly adsorbed carbon monoxide.

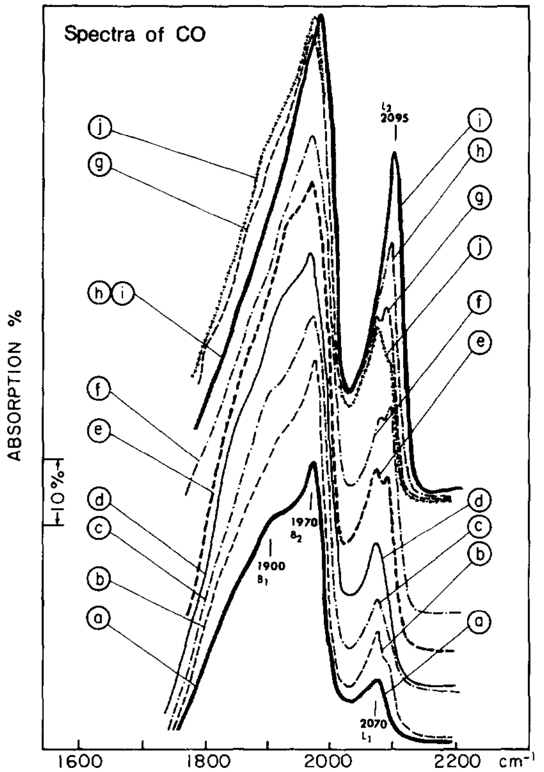


FIG. 2. Carbon Monoxide Adsorption at Room Temperature; a) After admission of 0.050 cc CO, b) Plus 0.040 cc CO, c) Plus 0.020 cc CO, d) Plus 0.040 cc CO, e) Plus 0.020 cc CO, f) Plus added CO (Pr = 5 × 10^{-2} mm), g) Plus added CO (Pr = 1 × 10^{-1} mm), h) Plus added CO (Pr = 4 mm), i) Plus added CO (Pr = 45 mm), j) Plus 15 minutes evacuation at room temperature. For clarity the vertical scale is displaced.

As the next three doses (b,c,d) are added the bands B_2 and L_1 both become more intense. The shoulder B_1 persists, but it does not seem to become more intense. Spectrum d corresponds to about 90% coverage with strongly bound CO. The next dose (e) was the last one in which the residual pressure (P_r) was at or below about 10^{-4} torr. In the corresponding spectrum (e) and those for subsequent doses, there is little further increase in the peak intensity of B_2 or L_1; hence, these species appear to have reached their saturation value. In spectrum (e), however, a new peak L_2 appears at 2095 cm^{-1}. With subsequent doses (f, g, h, i) this peak grows in intensity to the point where the lower intensity L_1 peak becomes first a shoulder on the L_2 peak and then even this shoulder disappears or becomes obscured by the intensive L_2 peak. Brief evacuation, however, restores the L_1 peak (j) with an intensity comparable to that when L_2 first appeared (e) and the more weakly bound L_2 is removed except for a slight shoulder on L_1.

As the peak L_2 develops there is little change in the peak intensity for B_2. There are, however, subtle changes in the band ascribed to the B species. First of all, as soon as the irreversible adsorption is complete (between spectrum e and f), the shoulder ascribed to B_1 disappears. As the L_2 species becomes more intense (h and i) the peak position for the B_2 species shifts up by about 10 cm^{-1}. It does so primarily by removal of intensity from the low frequency side of B and adding it to the high frequency side. Overall, the resulting band is sharper but the peak intensity undergoes little change. After evacuation (j) and removal of L_2, the B band shifts back and assumes the shape, position, and intensity it had before the development of the L_2 band.

If the reduced catalyst is briefly exposed to oxygen at room temperature so that chemisorption can occur, evacuated, and then exposed at room temperature to several torr of CO (more than enough for reaction plus saturation) spectra identical to that for the reduced sample are obtained. Moreover, carbon dioxide is formed in roughly the amounts expected from complete reaction with the adsorbed oxygen. Carbon dioxide yields no bands due to adsorbed species at moderate pressures. The spectrum of carbon monoxide (at low temperature) on a chemisorbed oxygen layer is different from that on a reduced surface (*22*); hence, we conclude that on the time scale of these experiments (i.e., the several minutes required for a scan), reaction of carbon monoxide with chemisorbed oxygen is very rapid and, with excess carbon monoxide, it goes to completion. This conclusion is similar to that reached in both classical adsorption studies (*23*) and LEED experiments (*18*).

If the surface is saturated with carbon monoxide, evacuated, and exposed to several torr of oxygen, the bands disappear completely on the time scale of the experiment. This is at variance with other authors: Kavtaradze *et al.* (*24*) report no effect on the spectra on exposure to 8 mm of oxygen at room temperature; Baddour *et al.* (*15*) state: "The room temperature spectrum was not altered by the presence or absence of oxygen in the gas phase." Classical adsorption studies also reveal that although the reaction occurs, there is a very long induction period (*23*). We have no explanation for this discrepancy. Our results do suggest, however, that both B and L forms react with oxygen readily at room temperature and at a rate quite a bit greater than that reported for platinum (*4*) at even higher temperatures (*25*).

We have also examined the spectrum when oxygen is presorbed on the catalyst and carbon monoxide is added in a series of doses in an attempt to titrate the surface oxygen. Part of the carbon monoxide reacts to form carbon dioxide and part adsorbs on the catalyst. The resulting spectra are different from those shown in Figure 2. Both the B and L bands are formed but they do not grow in step; with successive doses the relative increase in the B bands is greater than that of the L bands. Furthermore, the B band is broader and has its peak intensities at lower frequencies. Once an excess of CO is added, however, the spectrum resembles that in Figure 2 g-i.

Figure 3 shows the spectra obtained by

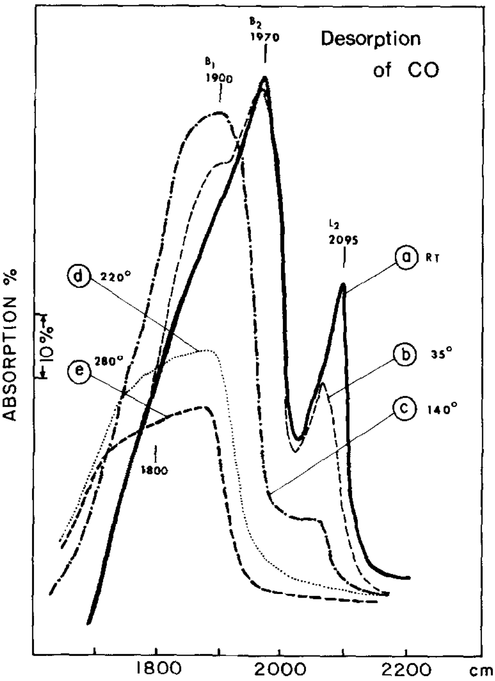


FIG. 3. Carbon Monoxide Desorption at Elevated Temperatures; a) CO adsorbed, PR = 10 mm, b) After 15 minutes evacuation at 35°C, c) After 90 minutes evacuation at 140°C, d) After 70 minutes evacuation at 220°C, e) After 60 minutes evacuation at 280°C.

desorption of carbon monoxide. To achieve reasonable rates of desorption, it was necessary to heat the catalyst in vacuo at successively higher temperature. First, the L bands essentially disappear and the B band shifts to the B_1 position (spectrum C). With higher temperature degassing (above 200°C) the B band becomes asymmetric and the peak shifts to frequencies below 1900 cm^{-1}. Comparison of Figure 2 and Figure 3 shows that *desorption process cannot concurrently reduce or remove the L and the B bands as in the sequence they form upon adsorption.*

The differences in the spectra for the adsorption sequence and the desorption sequence could be the result of structural changes in the adsorbed layer (or catalyst) accompanying the heating to effect desorption. To explore this possibility we carried out a series of experiments in which we dosed the catalyst with carbon monoxide, ran the spectrum, annealed the sample in a closed system at a higher temperature, and then cooled to room temperature and reran the spectrum. The results of these experiments are shown in Figure 4. Spectrum (a) corresponds to the spectrum after a 0.9 cc/g dose was added to the sample at room temperature. It corresponds well to the spectra obtained in Figure 2b; there is a B_2 band with the suggestion of a B_1 shoulder and an L_1 band. After standing for three hours at room temperature (b), there is some intensification of the B_1 shoulder and some decrease in the intensity of the L_1 band. When the sample was heated to 200°C, there was first a sudden increase in pressure to several microns followed by a slower fall lasting 5 to 10 minutes to about 10^{-4} torr or less. Spectrum (c) was obtained when the sample was cooled. The L_1 band has disappeared and the B band maximum was shifted to the B_1 position. A second dose (0.2 cc/g) was then added to the sample to yield the spectrum labelled d. Here we see the B_1 band of spectrum (c) slightly shifted to higher frequencies plus bands at the B_2 and L_1 positions. Annealing yields the same result as before: there is a burst of pressure followed by readsorption and the spectrum (e) after annealing yields essentially no L_1 band and a B band (intensified) at the B_1 position. Addition of a third dose yields spectrum f and causes the B_2 band to grow. Development of the B_2 band seems to occur by borrowing intensity from the low frequency side of the B_1 band. However annealing does not further effect any transition of L

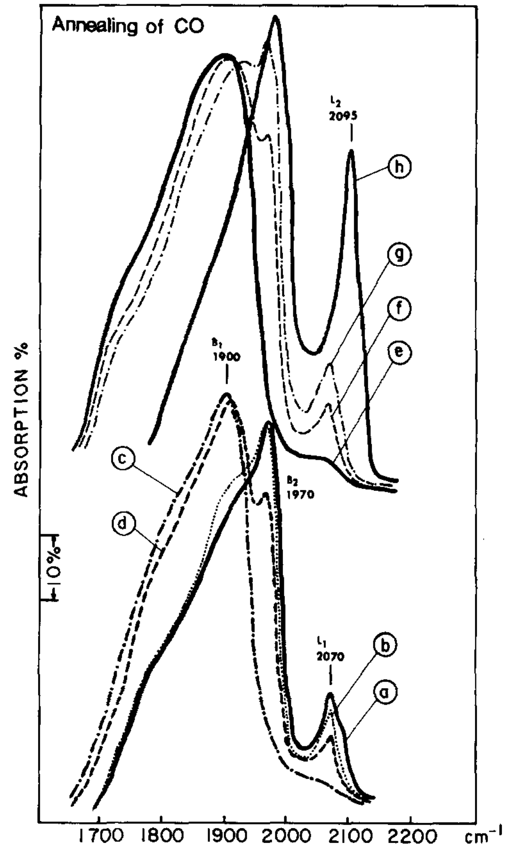


FIG. 4. Annealing of CO Adsorbed at Room Temperature, a) After admission of 0.090 cc at room temperature, b) After 3 hrs in closed system at room temperature, c) After 2 hrs in closed system at 200°C, d) After addition of 0.020 cc at room temperature, e) After 2 hrs in closed system at 200°C, f) After addition of 0.020 cc at room temperature, g) After addition of 0.020 cc at room temperature, h) After addition of CO to yield a pressure of 40 mm.

band into B band. Bands at the B_2 and L_1 positions grow with an additional dose (spectrum g). As saturation is approached (spectrum h), the B_1 band appears to shift and merge with the B_2 band. Annealing of the sample gives rise to a sudden increase in pressure but no readsorption. The spectrum at room temperature after annealing is the same as that before annealing.

In the above sequence a point is reached where the B bands seem to have achieved their maximum intensity. To reach such "saturation" a cumulative dose of about 1.1 cc/g is required. If we dose beyond this point, the linear band appears and grows, and B_2 forms at the expense of B_1. For the L_1 band to develop its maximum intensity requires another 0.6 cc/g which adsorbs essentially completely. Although these measurements are crude, they suggest that the ratio of B to L_1 species is about 2 to 1. Since the integrated intensity of the B_2 band is more than an order of magnitude greater than that for L_1, the extinction coefficient for the B band must be nearly an order of magnitude greater than that for the L_1 band.

Comparison of the isotherms to the data in Figure 4 permits us to make some assessment of the relative extinction coefficient of the L_2 band. In spectrum (h) the absorbance is about 0.3 for the L band whereas the maximum absorbance of the L_1 band is about 0.11 (spectrum d of Figure 1). Thus, the absorbance due to the L_2 species is about 0.2. The absorbance for the L_1 band stems from an estimated carbon monoxide adsorption of 0.6 cc/g whereas that for the L_2 band stems from the reversible adsorption of about 0.1 cc/g. Thus, it appears that the extinction coefficient for L_2 is about an order of magnitude greater than that for L_1.

Spectrum of CO on oxidized palladium. Figure 5 shows the spectra obtained for carbon monoxide (at 10 torr) adsorbed on the sample at room temperature after pretreating the sample in oxygen at successively higher temperatures. The spectra for samples oxidized at higher temperatures change with time due to slow reduction of the samples by carbon monoxide at room temperature. Thus, these spectra represent those taken immediately after CO adsorption. Examination of the hydroxyl region after hydrogen reduction following such pretreatment suggests the reducible oxygen is slightly greater at 140°C than at 35°C and that bulk oxidation is quite evident above 240°C and more complete at higher temperature. This result obtained *in situ* for the IR sample is wholly consistent with the isobar results illustrated in Figure 1. The spectra show that the effect of oxygen pretreatment (*11*) is insignificant at up to 180°C, presumably because the sur-

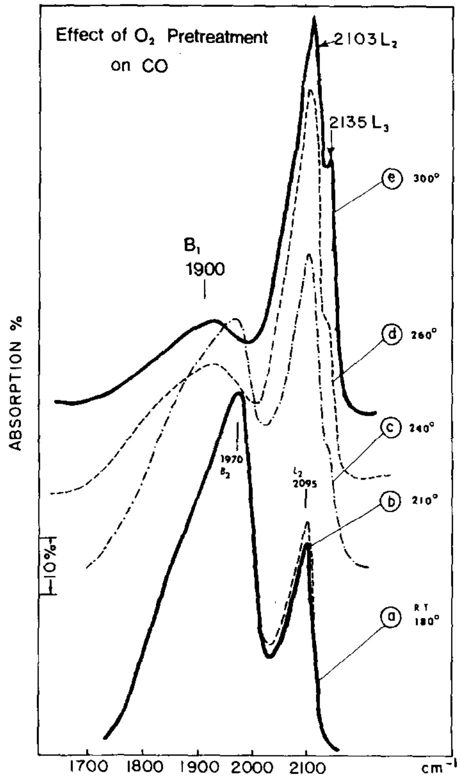


FIG. 5. Adsorption of Carbon Monoxide (10 mm) on Oxidized Palladium; a) Pretreatment room temperature, 100°C and 180°C, b) Pretreatment 210°C, c) Pretreatment 240°C, d) Pretreatment 260°C, e) Pretreatment 300°C.

face is immediately reduced by the excess carbon monoxide. Spectrum c, after pretreatment at 240°C, still shows bands at B_2 and L_2 positions, but the intensity of the L_2 band has been increased at the expense of B_2 band. Spectrum d, after pretreatment at 260°C, shows a further enhancement of the L_2 band with a slight shift to higher frequencies. The B band is now further reduced in intensity and shifted towards the B_1 position. In this spectrum we also see the development of a shoulder on the L_2 band at about 2135 cm^{-1}. Finally, after pretreatment at 450°C, the B band is almost gone and there are two linear species, an L_2 band shifted to 2103 cm^{-1} and an L_3 band at 2135 cm^{-1}.

DISCUSSION

Different spectra for the same coverage for adsorption versus desorption imply different species. Since desorption was achieved by heating, these differences may stem from thermally induced phase changes. If such phase changes occur, they appear to have the following characteristics:

1) They only occur in patches of chemisorbed carbon monoxide. Additional room temperature adsorption on the sites remaining after annealing, yields bands at the same positions found for adsorption prior to annealing.
2) They do not occur for a surface first saturated at room temperature.
3) They are reversed by adsorption of sufficient carbon monoxide to saturate the surface.

Although we cannot rule out phase changes with these characteristics, the restrictions are so severe that other explanations seem more plausible.

Adsorption to form the B_2 and L_1 bands is instantaneous on the time scale of these experiments even well below room temperature (*22*). Furthermore, up to the point of saturation of these sites, neither species is removed by brief evacuation (Figure 2j) and L_1 is diminished by prolonged (24 hr) evacuation. If adsorption is rapid and irreversible and diffusion into the center of the disk is somewhat slower, admission of a below-saturation dose may result in complete coverage at the outer edge of the disk with substantially no coverage in the interior of the disk. This is, for example, illustrated in Figure 6a. If the sample is heated to 200°C, desorption occurs as indicated by the observed pressure rise. Readsorption occurs in the interior of the disk and the net result is a change from hit-and-stick adsorption to adsorption on the strongest bonding sites with a consequent slow fall in pressure. After annealing, we approach the state represented by Figure 6b, wherein, in the limits, we have altered the adsorbed state from 100% coverage of 33% of the disk to 33% coverage of 100% of the disk. In the process (Figure 4b and

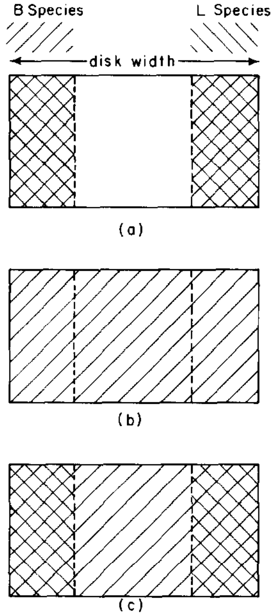


FIG. 6. Adsorption on a Catalyst Disk (Schematic); a) Adsorption of dose equal to 33% of saturation value, b) Above after annealing, c) (b) After another dose equal to 22% of saturation value.

c) we have transported the more weakly bound L_1 near the edge of the disk to the more firmly bound B species throughout the disk. A change in this direction occurs even on prolonged standing at room temperature (Figure 4a and b) as might be expected since L_1 must have some residual pressure to be slightly removed by prolonged evacuation. *We regard it as revealing that when the L_1 species is converted to B species by annealing, the band maximum for the bridged species shifts from the B_2 to the B_1 position. Apparently, B_2 is converted to B_1 in the absence of L_1.* If another below-saturation dose is added, we expect the result depicted in Figure 6c. In the interior of the disk we still have the B_1 species but the amount is less than in Figure 6b. At the outer edges of the disk we have the L_1 species and the B_2 species formed from B_1 species by the presence of L_1. In this case we would expect new bands at L_1 and B_2 with the B_2 bands formed by borrowing intensity from the B_1 band. This is the case in Figure 4d. Further annealling results again in the disappearance of L_1 and the consequent conversion of B_2 to B_1 (Figure 4e). Further dosing (Figure 4f-h) results in L_1 bands developing and B_2 borrowing intensity from B_1 until no B_1 band remains. After saturation of the entire disk, annealing should show a rise in pressure, but no fall, and the bands should show no further shift, as observed.

The description in Figure 6 applies only in the limit where adsorption is fast compared to diffusion. If this limit is not met, a gradient occurs in adsorption in the disk and a small dose should result in some bridged adsorption without L_1 species and some with L_1 species. Thus, we would expect to see both B_1 and B_2 bands in a nonlimiting case with the $B_2:B_1$ ratio a measure of how closely we approach the limiting case. The observation of only a slight B_1 shoulder on a much stronger B_2 peak in Figure 2a suggests that we are close to the limiting case depicted in Figure 6.

Results of carbon monoxide titrating experiments on an oxide covered surface support the above picture. Sub-saturation doses yield a spectrum in which B species (relative to L species) are more intensive. We believe this means that the reduction, although rapid, is slower than adsorption; hence, deeper penetration of the disk, prior to reduction and adsorption, results and leads to a spectrum closer to that for the annealed surface.

The conversion of B_1 to B_2 in the presence of L_1 suggests that B_1 and B_2 are not different species but that both bands stem from the same species; the different peak positions depend on whether or not L_1 species are present to interact with the B species. We also have some evidence (the desorption spectrum) that, as B_1 species are depleted, a further shift to lower frequencies occurs. Thus, the range of positions of the B bands can be rationalized by assuming a single species with interaction. Isolated B species have frequencies in the neighborhood of 1800 cm^{-1}; a surface saturated with B species has a band maximum at 1900 cm^{-1}; upon interaction with L_1 the bridged species shifts to 1970 cm^{-1}; upon interaction with L_2 the bridged species shifts to 1980 cm^{-1}. This shift in frequencies by intensity borrowing from broader low frequency bands to form sharper high frequency bands by interaction effects explains most of our observations.

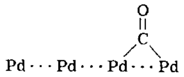
Such a hit-and-stick adsorption phenomenon as we have suggested has also been suggested by Eischens *et al.* (*5,29*) to explain the results of IR studies of adsorbed carbon monoxide on platinum. In their classic work dealing with carbon monoxide adsorption on palladium (*2*), however, this group found that room temperature adsorption and desorption produced comparable spectra. It is tempting to ascribe our disagreement with their work to differences in sample preparation; ours were compressed at relatively high pressures and compression has been shown to retard diffusion to and adsorption on supported palladium catalysts (*24*). This rationale, while comforting, does not explain the fact that Eischens *et al.* (*2*) found that the linear band "is removed immediately if the pressure is reduced to 10^{-4} torr" whereas we found that only prolonged evacuation had an effect on the L_1 band. Accordingly, we are forced to conclude that some other details in sample preparation or pretreatment yielded a catalyst on which carbon monoxide was more tightly bound than on the samples used by Eischens *et al.* (*30*).

Blyholder (*7*) has presented arguments that all adsorbed species are linear and differences in band position stem from π-bonding. We feel that the results for oxygenated samples suggest that the bands below 2000 cm^{-1} stem from bridged species. Observations with carbonyl complexes suggest that bridged bonds between two metal atoms are generally limited to derivatives of first-row transition metals (*6*). This restriction may stem from a requirement that the metal-metal distance be short enough so that the M-C-M angle is not too obtuse to be stable. In this event the first-row transition metals (radii about 1.24 Å) (*31*) are more suitable than members of the second and third row (radii about 1.34 Å) (*31*). With the second-row transition metals, e.g., rhodium (*32*), one finds bridge complexes involving bonding to three metal atoms in polynuclear complexes. In these complexes the metal-metal distance for atoms participating in the bridge is about 3% greater than that in the metal. Presumably, when this distance becomes substantially greater, bridge bonds become weaker. The isobars show that bulk oxidation occurs when palladium is treated with oxygen above about 240°C. If PdO is formed, the nearest Pd-Pd distance increases to a value 10% greater than that found for metals (*33*). This expansion in metal-metal distance could make bridge bonding impossible. In line with this it is found that when palladium is treated with oxygen under conditions such that bulk oxidation occurs, the B bands disappear and L bands intensify. Similar loss of B band intensity with retention or enhancement of L band intensity has been noted for mercury-poisoned (*10*), oxygen-treated (*34*) or copper-alloyed nickel (*14*), and Pd-Ag alloys (*35*). A similar interpretation could be invoked for these observations.

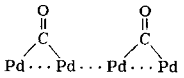
Our observations suggest that there are three different species (B, L_1 and L_2) responsible for the observed bands. The peak positions of the B band shift from below 1900 cm^{-1} to 1980 cm^{-1} as more carbon monoxide is added to the surface. If we assume that the position of the C—O stretching frequency, even for bridged species, is determined by the degree of back-bonding from appropriate d-orbitals, these shifts can be rationalized. On this basis the lower frequencies of B species are ascribable to more extensive metal-carbon π-bonding (*6*) which weakens the C—O bond. For the isolated B species, the back-bonding utilizes appropriately filled d-orbitals of the metal. If there are neighboring B species, there will be competition for electrons in d-orbitals and the amount of back-bonding will be reduced. Reduction of back-bonding via competition with neighbors will strengthen the C—O bond and increase the frequency. Upward frequency shifts should also be observed when L neighbors are introduced next to B species, but the interaction effect should produce more of a shift on the lower frequency, back-bonding B species than on the higher frequency L species, which has less back-bonding. Because of differing degrees of back-bonding, we would expect the B shifts for B-B neighbors to be greater than for B-L neighbors; actually, they appear to be comparable. Perhaps this is a reflection of the structure of the adsorbed species. LEED (*18*,*36*) results suggest that bridge species form a phase wherein no palladium atom forms more than one bridge and the surface is saturated with bridged species when the surface ratio of CO to Pd is 1/2 (*37*). In this case, for B species alone, back-bonding competition would have to occur indirectly via the bonding orbitals of neighboring metal atoms on the surface (*38*). After saturation of the surface with B species, L species could be formed only by placing a carbon monoxide on a palladium atom already participating in a bridge bond. In this event, even though the back-bonding of the L species was less, its interaction with the relevant orbitals of the metal would be direct and, hence, the shift could be comparable to that for B-B interaction.

In the above picture we have not paid any attention to the fact that different crystal faces and edges may occur. Most of the features we observe can be explained by the view that neighboring pairs of palladium atoms behave as if they were only loosely connected with their neighbors as suggested by Ertl and Koch (*18*). From this point of view, the adsorbed species can be represented as follows:

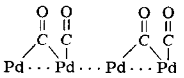
(a)



(b)



(c)



where a) represents an isolated B species (below 1900 cm^{-1}), b) represents the saturated B species (at 1900 cm^1), c) represents the surface saturated with B and L_1 species (*3*). This picture (highly schematic) has a stoichiometry which suggests a stoichiometry for chemisorption of approximately one carbon monoxide/surface palladium. The addition of a second linear carbon monoxide to the bridging pair may lead to the reversibly adsorbed species which gives rise to the L_2 band. This higher frequency intense band could be assigned to in-phase vibrations of the linear pair on the basis of coupling arguments akin to those used for carbonyl complexes (*8*); on this basis the band due to L_2 species would be more intense than that due to the L_1 species, as observed.

The above picture fits most of the available data for this catalyst. In one respect, however, it is deficient. Our estimates suggest that the ratio of L_1 species to B species is about 1 to 2. Structures that conform to this stoichiometry can be proposed (*38*) but they seem at variance with both LEED results and the overall adsorption stoichiometry. Accordingly, it seems prudent to take the view that our estimates of the amounts of L_1 and B demonstrate only that they are the same within a factor of two and that these estimates are too crude to define the stoichiometry.

Finally, we should like to emphasize that the spectrum obtained for carbon monoxide on palladium seems to be a sensitive function of the sample preparation and history (*12,15,16*). Accordingly, although we hope that our observations on this single sample contain some relevance for all supported palladium catalysts, we cannot expect our results will carry over *in toto* to all palladium catalysts.

ACKNOWLEDGMENT

One of us (A.P.) would like to acknowledge support by a UNESCO Fellowship while on leave from the Bulgarian Academy of Sciences. This work was partially supported by the Petroleum Research Fund administered by the American Chemical Society and also aided by funds from the National Science Foundation under Grant 34034X.

REFERENCES

1. Eischens, R. P., Pliskin, W. A., and Francis, S. A., *J. Chem. Phys.* **22**, 1786 (1954).
2. Eischens, R. P., Francis, S. A., and Pliskin, W. A., *J. Phys. Chem.* **60**, 194 (1956).

3. Eischens, R. P., *Z. Elektrochim.* **60,** 782 (1956).
4. Eischens, R. P., and Pliskin, W. A., *Advan. Catal.* **10,** 1 (1958).
5. Hammaker, R. M., Francis, S. A., and Eischens, R. P., *Spectrochimica Acta* **21,** 1295 (1965).
6. Abel, E. W., *Quart. Rev. Chem. Soc. 11,* 133 (1963).
7. Blyholder, G., *J. Phys. Chem.* **68,** 2772 (1964).
8. Cotton, F. A., and Kraihanzel, C. S., *J. Amer. Chem. Soc.* **84,** 4432 (1962).
9. Basila, M. R., *Appl. Spectroscopy Rev.* **1,** 289 (1968).
10. Yates, J. T., Jr., and Garland, C. W., *J. Phys. Chem.* **65,** 617 (1961).
11. Garland, C. W., Lord, R. C., and Triano, P. F., *J. Phys. Chem.* **69,** 1188, 1195 (1965).
12. Van Hardeveld, R., and Hartog, F., *Advan. Catal. Relat. Subj.* **22,** 75 (1972).
13. Clarke, J. K. A., Farren, G., and Rubalcava, H. E., *J. Phys. Chem.* **71,** 2376 (1967).
14. Hobert, H., *Z. Chem.* **6,** 73 (1966).
15. Baddour, R. F., Modell, M., and Heuser, U. K., *J. Phys. Chem.* **72,** 3621 (1968).
16. Baddour, R. F., Modell, M., and Goldsmith, R. L., *J. Phys. Chem.* **74,** 1787 (1970).
17. Throughout this paper we shall accept the assignments of Eischens, Francis and Pliskin (*2*), i.e., bands below 2000 cm^{-1} will be termed bridged (or more simply, B) species and bands above 2000 cm^{-1} will be termed linear (or more simply, L) species.
18. Ertl, G., and Koch, J., paper No. 70 presented at the Vth International Congress on Catalysis, August 21–25, 1972, Palm Beach, Florida.
19. Schrieffer, J. R., *J. Vac. Sci. Techn.* **9,** 561 (1972).
20. Palazov, A., and Shopov, D., *Commons. Dept. Chem. Bulg. Acad. Sci.* **1,** 175 (1968).
21. Aben, P. C., *J. Catalysis* **10,** 224 (1968).
22. Unpublished results, A. Palazov and C. C. Chang.
23. Stephens, S. J., *J. Phys. Chem.* **63,** 188 (1959).
24. Kavtaradze, N. N., Boreskova, E. G., and Lygin, V. I., *Kinet. Catal.* **2,** 349 (1961).
25. Heyne, H., and Tompkins, F. C., *Proc. Roy. Soc. A* **292,** 460 (1966).
26. Gruber, H. L., *J. Phys. Chem.* **66,** 48 (1962).
27. Sinfelt, J. H., *Catalysis Rev.* **3,** 175 (1969).
28. In the course of these studies we discovered an effect which we would like to note but shall not attempt to explain. When the palladium sample is oxidized, there is an immediate loss of transmission. The transmission is immediately restored when carbon monoxide is adsorbed even though the accompanying reduction is confined to the surface layer.
29. Eischens, R. P., *Accounts Chem. Res.* **5,** 74 (1972).
30. The irreversibility of CO adsorption found in isotherm measurements on the large sample agrees with this conclusion based on IR studies.
31. Bond, G. C., "Catalysis by Metals," pp. 489–491. Academic Press, New York, 1962.
32. Corby, E. R., Dahl, L. F., and Beck, W., *J. Amer. Chem. Soc.* **85,** 1202 (1963).
33. Moore, W. J., Jr., and Pauling, L., *J. Amer. Chem. Soc.* **63,** 1392 (1940).
34. O'Neil, C. E., and Yates, D. J. C., *Spectrochimica Acta* **17,** 953 (1961).
35. Soma-Noto, Y., and Sachtler, W. M. H., *J. Catalysis* **32,** 315 (1974).
36. Park, R. L., and Madden, H. H., *Surf. Sci.* **11,** 188 (1968).
37. Bond, G. C., *Disc. Faraday Soc.* **41,** 200 (1966).
38. Rhodium, the periodic chart neighbor of palladium, forms a cluster compound $Rh_6(CO)_{16}$[32] in which the six-metal atoms are at the corners of an octahedron with a metal-metal distance of 2.78 compared to 2.68 Å in the metal. Accordingly, this compound would seem a good model for a supported face-centered cubic metal crystallite with exposed 111 faces in the limit of very small particle size. In the rhodium complex, the bridged carbon monoxides are above the faces of the octahedron and bond to three metal atoms. By analogy, therefore, we cannot exclude the possibility that species B on palladium forms bonds to three surface metal atoms. Such a picture, however, seems to be at variance with the LEED results.