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Internal Reflection Spectroscopy of Adsorbed Molecules on Metal Films: Carbon Monoxide on Palladium

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A brief discussion of the advantages and problems experienced in the study of adsorption on metal films using infrared internal reflection spectroscopy (IRS) is given. The structure of adsorbed carbon monoxide on palladium was examined using polarized IRS. It is shown that adsorbed carbon monoxide which gives rise to infrared bands above 2000 cm^{-1} are structure insensitive while those species that absorb below 2000 cm^{-1} are structure sensitive (form preferentially on certain portions of small palladium crystals). It is proposed that the species which forms with a high heat of adsorption (> 40 kcal/mole) and absorbs at low frequency (< 1800 cm^{-1}) involves bonding of both carbon and oxygen to palladium atoms on a low index face.

INTRODUCTION

Infrared internal reflection spectroscopy (IRS) must be considered a technique which supplements the information obtained by conventional infrared transmission experiments (*1,2*). If the material to be studied is available in a high area form or can be dispersed on a high area material transparent in the frequency range of interest, the simplicity of conventional transmission spectroscopy dictates its use. IRS has a unique advantage when the adsorbing surface is not available in a high-area form, e.g., single crystal oxides (*3*). It can also be used to extend the accessible frequency range below the transparency limits of the much used high-area supports, silica and alumina. That is, materials which have good infrared transmission properties (NaCl, KBr, CsI) cannot be obtained in stable high-area form but do make useful internal reflection prisms on which films can be supported. When the surface under investigation is a single crystal or an oriented film, polarized IRS provides information not usually obtainable using transmission spectroscopy (*4*). It is this latter property of IRS which we exploit in the present study and which allows us to make new observations concerning the structure of adsorbed CO on palladium, a system which has been investigated by infrared spectroscopy many times since the original study of Eischens *et al.* (*5*) some 20 yr ago.

By analogy with spectra of metal carbonyls of known structure, Eischens *et al.* (*6*) suggested a linear structure with CO bonded to a single surface atom to account for bands above 2000 cm^{-1} and assigned bands below 2000 cm^{-1} to a bridged structure with CO bonded to two metal atoms. Moreover, it was concluded in this original work that the surface of Pd (and Ni) is heterogeneous; "the surface is divided into two or three major components" each of which has a distribution of sites (*6*). The linear/bridged bonded interpretation has been questioned, particularly by Blyholder (*7*), but it is now generally accepted. In their recent study of Pd–Ag alloys, Soma-Noto and Sachtler (*8*) showed that the linear CO bonded to a single Pd atom is insensitive to both the geometric and electronic structure around the Pd atom. Palazov *et al.* (*9*) [as well as Soma-Noto and

Sachtler (*8*)] argue that the bands between 1900 and 2000 cm^{-1} are due to bridged carbon monoxide interacting with neighboring bridged and/or linear species.

We present evidence from polarized IRS that the linear CO structure is adsorbed on all exposed crystal planes while the bridged species is structure sensitive not only in the sense that two Pd spaced at about 2.73 Å are required (*10*) but is also structure sensitive in the sense that it is preferentially adsorbed on certain planes of small palladium crystals. In addition we propose a new structure for the CO species which absorbs below 1800 cm^{-1}.

EXPERIMENTAL SECTION

Apparatus and materials. The internal reflection cell and other equipment used were essentially the same as that described in a previous study (*4*). The metal film deposition was performed in a Veeco Model VE-400 evaporation station using a molybdenum evaporation boat with an alumina-coated crucible to hold the palladium to be evaporated. Palladium sponge, 99.9995% pure, was used as an evaporation source. A quartz crystal monitor was used to measure film thickness. No correction has been made for the difference in the sticking probability for NaCl and Pd covered quartz in the first monolayer of metal layed down.

Alkali halide internal reflection prisms were 52 × 20 × 1 mm beveled to 45° (~ 50 reflections). Sodium chloride and potassium bromide single crystals were cut and polished by Harrick Scientific Corp. or Wilks Scientific Corp., both boules grown from the melt (Czochraliski) by Optivac. Laue X-ray photographs confirmed that NaCl and KBr single crystals were oriented with their major faces parallel to the (100) natural cleavage plane. Carbon monoxide was Matheson CP grade and was used as supplied.

Procedure. The alkali halide substrate was outgassed at 400–500°C in 10^{-6} Torr vacuum for several hours, cooled to room temperature and a full spectrum was recorded before transfer to the evaporation station. The transferral between cell and evaporation required 2–4 min exposure to air. Films were deposited on both major faces of the substrate. The metal source material in the evaporation boat was heated to just below its melting point over a period of roughly 30 min in order to degas the metal, then heated at the desired evaporation temperature for 2 min before the shutter was moved to expose the substrate. Exposure times ranged between 5 and 15 sec and evaporation rates were estimated to be 2–5 Å/sec on the basis of change in frequency of the quartz crystal monitor.

RESULTS AND DISCUSSION

The internal reflection prisms, as received, exhibit water and hydrocarbon bands of varying intensity and certain other impurity absorptions in the 1100^{-1} cm frequency range as shown in Fig. 1a for NaCl. Following an outgassing at 400–500°C at 10^{-6} Torr vacuum for several hours, the water and hydrocarbon were removed from the NaCl surface and the background spectrum was reasonably flat, Fig. 1b. Also shown (Fig. 1c) is the spectrum of a Pd film deposited on NaCl at a nominal thickness of 25 Å. When the Pd film thickness was increased to 100 Å, it became completely adsorbing over the entire frequency range, but could be made transparent by oxidation of the metal film at high temperature. All films used for CO adsorption studies were thinner than that used to obtain the spectrum shown in Fig. 1c. These very thin films exhibited a background essentially identical to that of the internal reflection prism without a film except that the transmission was decreased a few percent.

Following reduction with hydrogen at room temperature and evacuation to $<10^{-6}$ Torr, admission of 5.5 Torr CO

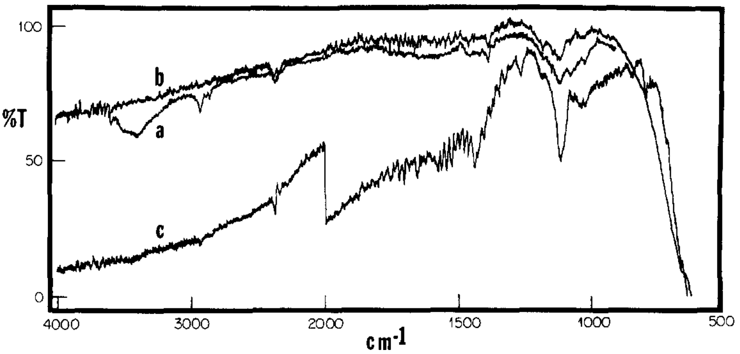

FIG. 1a. Background spectrum of NaCl internal reflection prism as received. (b) Background spectrum of NaCl after evacuation at 500°C. (c) Spectrum of 25 Å Pd film on NaCl. Note scale change at 2000 cm^{-1}. The major impurity bands between 1100 and 1200 cm^{-1} are assigned to surface sulfate, see App. 5 of Ref. (*18*).

resulted in the spectrum shown in Fig. 2a for a very thin Pd film supported on KBr. This spectrum is similar to that reported by Eischens *et al.* (*5*) for Pd on silica. As reported previously (*5*) the band above 2000 cm^{-1} is immediately removed upon evacuation while the bands below 2000 cm^{-1} are not. Exposure to oxygen after evacuation at room temperature removes all CO bands and results in a flat background with no evidence for surface carbonate formation. When the room temperature oxidized Pd film is again exposed to CO, the band above 2000 cm^{-1} is much diminished and the band maximum below 2000 cm^{-1} is shifted to lower frequency as shown in Fig. 2b at a pressure of 2.4 Torr CO. Admission of oxygen to a pressure equal to that of CO does not much change the spectrum when the Pd film has been previously oxidized. These results are in qualitative agreement with that of Baddour *et al.* (*11*), but the band shapes and relative intensities are quite different.

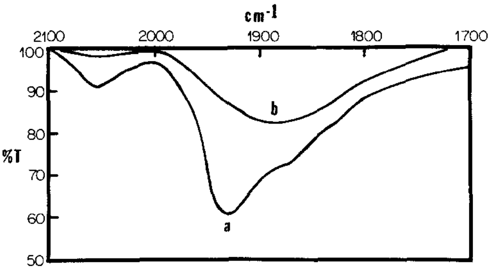

FIG. 2a. Carbon monoxide (5.5 Torr) adsorbed on a hydrogen reduced Pd film supported on KBr. (b) Carbon monoxide (2.4 Torr) adsorbed on an oxidized Pd film.

The results in Fig. 2 are reproducible and it is possible to cycle between the (a) and (b) by repetitive reduction with hydrogen or oxidation with oxygen at room temperature. That is, the films appear to be stable with respect to sintering at room temperature, but they are also contaminated by hydrocarbon (analyzed by IRS) and neither reduction or oxidation at room temperature will remove the hydrocarbon impurities. Outgassing at 400–450°C removes the hydrocarbon, but results in a film which is nearly inert to CO adsorption. Reduction in hydrogen (or CO) at 200–300°C will reactivate the film, in part, to CO adsorption. Because of the stability and relatively intense spectra obtained using films treated at room temperature, we choose to analyze the results of these films using polarized IRS.

We have deliberately prepared very thin Pd films which are discontinuous. They are expected to behave as dielectrics (*12*), i.e., they have very small values of the attenuation index k, and n varies very little with frequency where k and n are defined by the complex refractive index $\hat{n} = n(1 - ik)$. The fact that our films absorb only a few percent following 50 reflections and the film spectrum follows the contour of the spectrum of the clean KBr prism confirms that our films have the above mentioned properties. But in order to use the simple equations developed by Harrick (*13*) for calculating relative electric field amplitudes in the thin film, it is still necessary to have a value for n_2, the effective index of refraction of the metal film.

We take advantage of the presence of the hydrocarbon impurity to calculate n_2. That is, from the measured ratio of absorbance for perpendicular and parallel polarization,[1] the effective index of refraction of the metal film can be calculated from the equation,

$$\frac{A_\perp}{A_\parallel} = \frac{(1 + n_{31}^2)\sin^2\theta - n_{31}^2}{(1 + n_{32}^4)\sin^2\theta - n_{31}^2}, \qquad (1)$$

where $n_{31} = n_3/n_1$, the ratio of refractive indexes in vacuum and KBr; $n_{32} = n_3/n_2$ and θ is the angle of incidence. Equation (1) is not easily applied directly to the metal film since the absorbance is very small and $A_\perp/A_\parallel$ would be very much changed by small changes in background transmission due to optical alignment, spectrometer characteristics, etc., when the KBr prism is removed to deposit the film and replaced in the cell. These problems are not present for the hydrocarbon band where $A_\perp/A_\parallel$ is measured relative to the flat background of the metal film. But as discussed below, the film is not composed of randomly oriented crystallites and therefore Eq. (1) can only be applied to an absorption that is indpendent of orientation effects. We have previously shown that the asymmetric CH_3-stretch is insensitive to orientation effects, even when attached to molecules which are well oriented on the surface of a single crystal (*4*). Therefore $A_\perp/A_\parallel = 1.77$ observed for asymmetric stretch of impurity CH_3-groups was used to calculate $n_2 = 1.5$.

If the Pd crystallites were in fact randomly oriented, then the absorbance ratio for all bands would be equal to 1.77 even if absorption occurred on specific crystal planes of the randomly oriented Pd crystallites. The measurement of $A_\perp/A_\parallel$ as a function of frequency for the absorption bands of absorbed CO, Fig. 3, indicates that there exists some net orientation of the Pd crystallites with respect to the surface of the KBr prism and that the different CO species (which absorb at different frequencies) do not absorb uniformly on all exposed crystal planes. The behavior of the CO species absorbing above 2000 cm^{-1} is different. At saturation coverage the $A_\perp/A_\parallel = 1.7$ and is constant across the band suggesting a single species rather uniformly adsorbed on all exposed crystal planes.

We now attempt a more specific interpretation of the data given in Fig. 3. The error bars are large outside the central portion of the absorption band, but it is clear that the $A_\perp/A_\parallel$ exceeds the random ratio, 1.77, over most of the band and probably increases to about 4 below 1800 cm^{-1}. The maximum value that $A_\perp/A_\parallel$ may

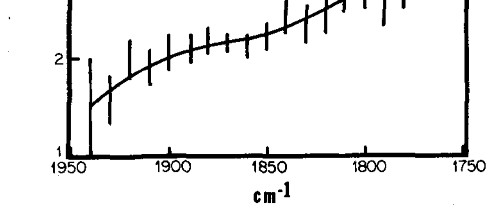

FIG. 3. The ratio of perpendicular to parallel absorbance for absorbed CO, Fig. 2a, as a function of frequency.

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[1] Perpendicular and parallel polarization are defined with respect to the plane of incidence and reflection of the transmitted beam.

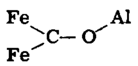
have would be attained when the dipole of the absorbing CO molecules is parallel to the internal reflection prism, in the *xy* plane, where

$$\frac{A_\perp}{A_\parallel} = \geqslant \frac{E_y^2}{E_x^2} = \frac{(1 + n_{31}^2)\sin^2\theta - n_{31}^2}{\sin^2\theta - n_{31}^2} = 5.0. \tag{2}$$

The equal sign applies for a random orientation in the *xy* plane. It should be noted that Eq. (2) does not involve the index of refraction of the metal film since the tangential components of the electric field must be continuous across an interface. It is also important to observe that Eq. (1) reduces to Eq. (2) when the index of refraction of the metal film becomes very large. That is, the interpretation that the change in $A_\perp/A_\parallel$ shown in Fig. 3 is due to orientation effects would not be valid if n_2 became large in the frequency range 2000–1700 cm^{-1}. Theoretically, this is not expected and we have made two experimental observations that indicate that a changing n_2 is not the correct explanation for the results given in Fig. 3. The first observation is that $A_\perp/A_\parallel$ is a function of CO coverage in the frequency range 1950–1900 cm^{-1}, increasing when the coverage is increased (pressure is increased above 0.005 Torr) and decreasing as the coverage is reduced. It follows that this is an orientation effect, i.e., CO cannot be inducing a change in the effective index of refraction of the metal film since then $A_\perp/A_\parallel$ should change in the 1900–1750 cm^{-1} range as well as the range above 1900 cm^{-1}. The second observation is that $n_2 \leqslant 1.5$ when the band near 1600 cm^{-1} due to surface formate (adsorption of formic acid) is used to calculate n_2 using Eq. (1). Therefore we conclude that the adsorbed CO giving rise to absorption below 1800 cm^{-1} is a result of a preferential alignment of the CO dipoles parallel to the surface of the KBr internal reflection prism.

While our optical data allows us to deduce that small Pd crystals have some net orientation on the KBr (or NaCl) single crystals, we have not been able to determine the orientation directly. It is well known that Pd forms films with parallel planes with parallel directions on air-exposed (001) NaCl substrates when the film is thick enough to form a single-crystal film (14). The work of Murr (*15*) indicates that continuous and single-crystal films occur at a film thickness of 200 Å. Moreover, there is evidence from his work for bcc and simple-cubic crystallography within approximately 10–15 atomic layers of the (001) NaCl substrate. These effective crystal structures arise during the initial nucleation on the substrate and may be accounted for by rotation of the nuclei having thickness of only a few atom layers about the perpendicular to the substrate surface. In any case, it appears reasonable to assume that the relatively slow evaporation rate and low vacuum used in this work would result in homogeneously nucleated crystallites with a net orientation of a low index face parallel to the substrate surface.

Eischens *et al.* (*5*) proposed that adsorbed CO species which absorb at frequencies below 2000 cm^{-1} involve bridge bonding to CO between two (or more) Pd atoms, a view which is reinforced by the recent work of Soma-Noto and Sachtler (*8*) on Pd–Ag alloys. A bridge structure that would be consistent with the high heat of adsorption (>40 kcal/mole) (*8*), low frequency (<1800 cm^{-1}) and presumed orientation of Pd crystallites would involve bonding of both carbon and oxygen to Pd surface atoms on a low index face of the Pd crystallite which is parallel to the KBr substrate. Such a structure has been proposed for the 1620 cm^{-1} band observed for Ni films evaporated in the presence of CO (*16*). Moreover, coordination through both carbon and oxygen of this kind,



is known in

$$Fe_2(\pi C_5H_5)_2(CO)_2[COAl(C_2H_5)_3]_2$$

and the infrared frequency for this bridged CO is 1682 cm^{-1} (*17*). It is, of course, impossible to give an unambiguous interpretation of the very high $A_\perp/A_\parallel$ ratio at low frequency without independent knowledge of orientation and shape of the Pd crystallites. For example, Eq. (2) would also apply to CO bonded through carbon only to Pd atoms on the crystallite sides which are perpendicular to the KBr prism surface. But, such an interpretation leaves open the question of how the low frequency (< 1800 cm^{-1}) bridged CO is to be distinguished from those bridged CO species that absorb above 1800 cm^{-1}. Therefore, we believe that the most probable structure for the most strongly bound adsorbed CO absorbing at the lowest frequency is one bonded through both carbon and oxygen on a low index Pd surface oriented parallel to the KBr prism surface.

The bonds between 1800 and 2000 cm^{-1} must still be attributed to a bridge bonded CO involving two (or more) Pd atoms. For these bonds, our results are consistent with the recent interpretation of Palazov *et al.* (*9*), i.e., most of the changes with coverage reflect changes in the degree of interaction with coverage. But since the polarization ratio is always different from the random value (and a function of coverage between 1900 and 1950 cm^{-1}), certain planes (and/or edges) of the crystallites must be preferentially covered. Therefore we conclude that the linear bonded CO absorbs on single Pd sites randomly (structure insensitive adsorption) but all bridged bonded CO adsorb on pair sites specific to given planes (edges) of the Pd crystal (structure sensitive adsorption).

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