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The adsorption and structure of carbon monoxide on ethylidyne-covered Pd(1 1 1)

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Abstract

A quarter of a monolayer of carbon monoxide (CO) adsorbs on ethylidyne-covered Pd(1 1 1) (ethylidyne saturation coverage, 0.25 monolayers) at 300 K, compared to the saturation coverage of 0.55 monolayers for CO on clean Pd(1 1 1). Infrared and temperature-programmed desorption data reveal that CO adsorbs on the hexagonal-close-packed, threefold hollow site on ethylidyne-covered Pd(1 1 1). This, in turn, suggests that ethylidyne species on Pd(1 1 1) occupy face-centered-cubic, threefold hollow sites. Atop sites become occupied when an ethylidyne-covered Pd(1 1 1) surface is pressurized with 10^{-2} Torr of CO, and no additional CO appears to adsorb when the surface is pressurized with 5 Torr of CO. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is now well established that the surface of many transition-metal catalysts are covered by relatively strongly bound carbonaceous layer during reaction. For example, noble-metal ethylene hydrogenation catalysts are covered by ethylidyne species (CH_3–C≡) [1] and Pd(1 1 1)-catalyzed acetylene cyclotrimerization [2] proceeds in the presence of a vinylidene (CH_2=C=) layer [3]. It has been shown in the case of vinylidene-covered Pd(1 1 1) that molecules can adsorb onto the palladium surface when pressurized, in spite of the presence of this layer [4]. It has further been demonstrated that benzene is formed by a reaction between adsorbed acetylene and vinylidene [5] species so that these carbonaceous layers are not necessarily inert spectator species but can participate in catalytic reactions. We have previously used carbon monoxide (CO) as a probe molecule for studying adsorption onto these carbonaceous-layer-covered surfaces under moderate and high pressures [6]. One advantage to using CO for this purpose is that the chemistry of this molecule has been intensively investigated on clean transition-metal surfaces [7] and it has a large infrared absorption cross-section. Furthermore, the CO stretching frequency is sensitive to the surface adsorption site [8]. In the following, infrared spectroscopy, temperature-programmed desorption and molecular beam methods are used to probe

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CO adsorption on ethylidyne-covered Pd(1 1 1). CO adsorption, in this case, is substantially different to that on the vinylidene-covered surface, primarily because of the different saturation coverages of the two species where Θ_{sat}(vinylidene) ~ 1 monolayer on Pd(1 1 1) [2] (where coverages are referenced to the palladium site density on the (1 1 1) surface) whereas an ethylidyne-saturated surface is more open, with a saturation coverage of 0.25 monolayers (see below).

2. Experimental

Experiments were carried out in two stainless-steel, ultrahigh vacuum chambers operating at base pressures of $\sim 8\times10^{-11}$ Torr following bake-out and which have been described in detail elsewhere [4,9]. Infrared data were collected from a palladium single crystal sample mounted in a modified 2 3/4″ six-way cross equipped with infrared-transparent, KBr windows. The sample could be resistively heated to 1200 K or cooled to 80 K using liquid nitrogen. Light from a Bruker Equinox infrared spectrometer passes through a polarizer and is focused on the sample at an incidence angle of ~80° and the reflected light steered onto the detector of a liquid-nitrogen-cooled, mercury cadmium telluride detector. The complete light path is enclosed and purged with dry, CO_2-free air. Data were typically collected for 1000 scans at 4 cm^{-1} resolution.

Molecular beam experiments were carried out in an 8″ diameter, stainless-steel vacuum chamber pumped by means of a 6″ diameter, liquid-nitrogen trapped diffusion pump (pumping speed 850 l/s). The Pd(1 1 1) sample is mounted to a carousel geometry manipulator which allows the sample to be moved in and out of the beam. The sample can be resistively heated to 1200 K, and cooled to 80 K by thermal contact to a liquid nitrogen-filled reservoir. The chamber also houses a Dycor quadrupole mass spectrometer which is under computer control and can sequentially monitor the intensity of up to five masses. This is used for leak testing, gauging the purity of gases, temperature-programmed desorption experiments and for measuring the background pressure during a molecular beam experiment. Background pressures are also monitored by a nude ionization gauge located in both chambers and all pressures are uncorrected for ionization gauge sensitivities.

The sample is cleaned using a standard procedure which consists of heating at 1000 K in $\sim 4 \times 10^{-8}$ Torr of oxygen and then annealing at 1200 K in vacuo to remove any remaining oxygen. Since the carbon KLL Auger feature is effectively obscured by a strong palladium peak, Auger spectroscopy is not particularly sensitive to the presence of small amounts of carbon on the surface. It was found that a more sensitive gauge of carbon coverage was to saturate the surface with oxygen and to perform a temperature-programmed desorption experiment. The presence of surface carbon is manifest by the desorption of CO. As the surface becomes depleted of carbon, the CO yield decreases and the yield of oxygen increases correspondingly in intensity. The complete absence of carbon is indicated by the desorption of only O_2.

Ethylene (Matheson) and CO (Linde, Research Grade) were transferred to glass bottles and attached to the gas-handling system of the vacuum chambers. Ethylene was further purified by several freeze–pump–thaw cycles and CO was dosed while a cold finger on the glass bottle was immersed in liquid nitrogen to trap any less volatile components (e.g., carbonyls). The cleanliness of both reactants was monitored mass spectroscopically.

3. Results

A series of temperature-programmed desorption spectra of ethylene adsorbed on Pd(1 1 1) at 300 K are shown in Fig. 1. It has been shown previously that this leads to the formation of an ethylidyne overlayer [10]. Only hydrogen (2 amu) was detected exhibiting a peak centered at ~425 K indicating that ethylidyne thermally decomposes at this temperature. A smaller feature is noted at ~360 K at low exposures (~2.5 L) and the temperature of this state decreases with increasing exposure.

As noted above, CO has been used to probe the way in which sites are blocked by the presence of

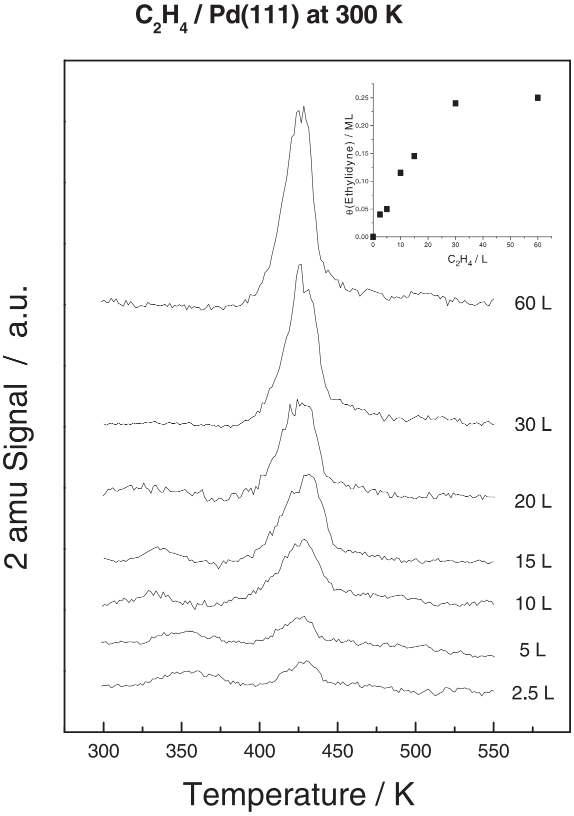

Fig. 1. 2 amu (hydrogen) temperature-programmed desorption spectra of ethylene adsorbed on Pd(1 1 1) at 300 K as a function of ethylene exposure. Exposures are marked adjacent to the corresponding spectra. Shown as an inset is the hydrogen desorption yield plotted versus ethylene exposure where the ordinate has been converted into ethylidyne coverage by comparison with the desorption yield of a saturated overlayer of hydrogen on Pd(1 1 1).

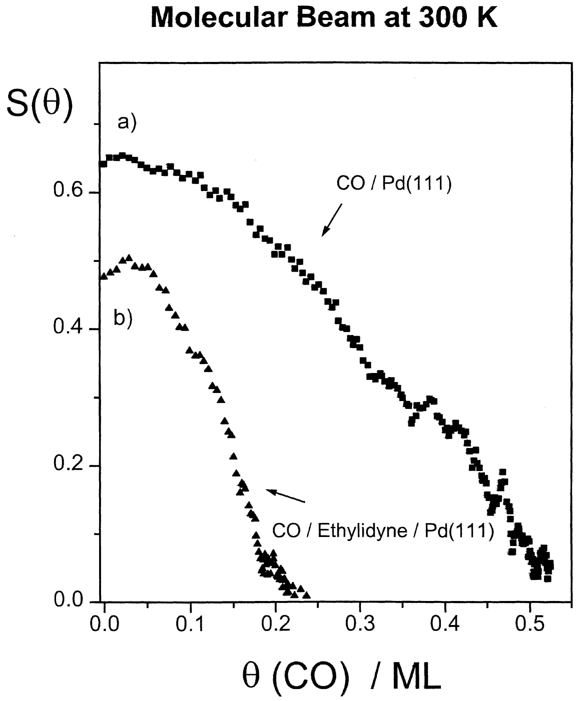

Fig. 2. Plot of sticking probability versus coverage for (a) CO on clean Pd(1 1 1) at 300 K and (b) CO adsorption on ethylidyne-covered Pd(1 1 1), both measured using the King and Wells method [11].

the carbonaceous layer. No CO adsorbs on a vinylidene-covered surface in ultrahigh vacuum [4]. In contrast, substantial amounts of CO can adsorb onto ethylidyne-covered Pd(1 1 1) as indicated by the data in Fig. 2. This compares the sticking probability versus coverage, measured using the King and Wells method [11], for CO on clean Pd(1 1 1) at 300 K (Fig. 2(a)) with that for CO on an ethylidyne-saturated surface (Fig. 2(b)). The saturation coverage of CO on Pd(1 1 1) at 300 K is 0.55 monolayers [12]. Using this calibration reveals that the saturation CO coverage on ethylidyne/Pd(1 1 1) in ultrahigh vacuum is 0.23 ± 0.02 monolayers and demonstrates that ethylidyne leaves a substantial portion of the surface accessible to CO, implying that its effectiveness in blocking CO adsorption is substantially smaller than that for vinylidene-covered Pd(1 1 1). Fig. 3 displays the corresponding temperature-programmed desorption spectra. The 2-amu spectrum has shifted slightly from 425 (Fig. 1) to ~455 K in the presence of CO indicating that ethylidyne decomposition is inhibited by the presence of CO. The ratio of the areas of the 28-amu desorption profiles for clean Pd(1 1 1) (Fig. 3(a)) to that for the ethylidyne-covered surface (Fig. 3(b)) is 2.0 ± 0.1, in good agreement with the relative saturation coverages found using molecular beam methods (Fig. 2). The low-temperature (360 K) CO desorption state is only slightly affected by the presence of an ethylidyne overlayer whereas the high-temperature (460 K) state is substantially smaller.

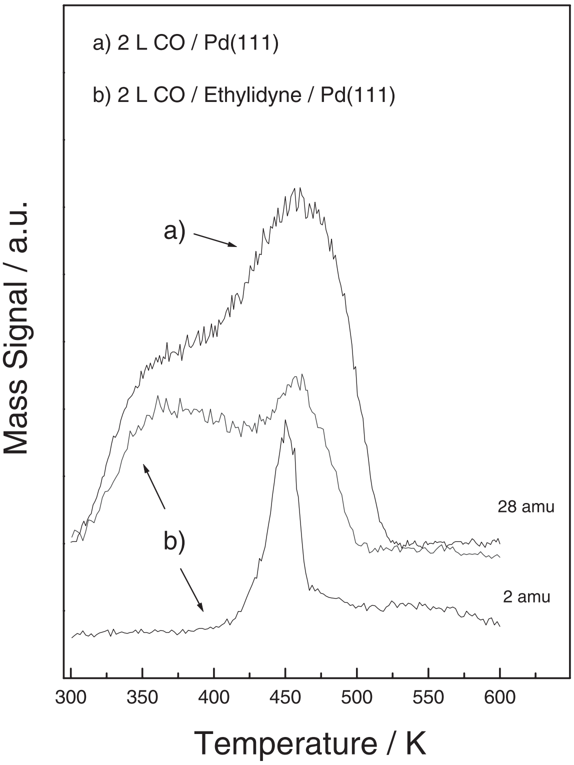

Fig. 3. Temperature-programmed desorption spectra for (a) CO on clean Pd(1 1 1) monitoring 28 amu (CO) and (b) CO on ethylidyne-covered Pd(1 1 1) monitoring 28 (CO) and 2 (H_2) amu. The CO exposure was 2 L in each case.

The corresponding reflection–absorption infrared spectra (RAIRS) are displayed in Fig. 4. In all cases, a feature at ~1330 cm^{-1} is due to the methyl bending mode of ethylidyne (Fig. 4(a)) [13]. This shifts slightly to ~1338 cm^{-1} in the presence of a high pressure of CO (Fig. 4(b) and (c)). It is also broadened somewhat when pressurized to 5 Torr (Fig. 4(c)), an effect that has been noted previously for the adsorption of ethylene on ethylidyne-covered Pd(1 1 1) [9]. CO exhibits an intense feature at 1907 cm^{-1} following a 2 L CO exposure with a smaller feature present at ~2050 cm^{-1}. Pressurizing the surface with 10^{-2} Torr of CO causes the 1907 cm^{-1} feature to shift to 1940 cm^{-1}, and the 2050 cm^{-1} peak to move to 2080 cm^{-1}. In addition, the intensity of the 1940 cm^{-1} feature is 1.6 ± 0.1 times larger than the 1907 cm^{-1} peak and the 2080 cm^{-1} peak is substantially larger than that at 2050 cm^{-1}. Further increasing the pressure to 5 Torr (Fig. 4(c)) causes the 1940 cm^{-1} feature to shift to ~1946 cm^{-1}, although the intensity of this feature is not measurably affected. Note that the gas-phase CO signal has been subtracted from the spectrum in Fig. 4(c).

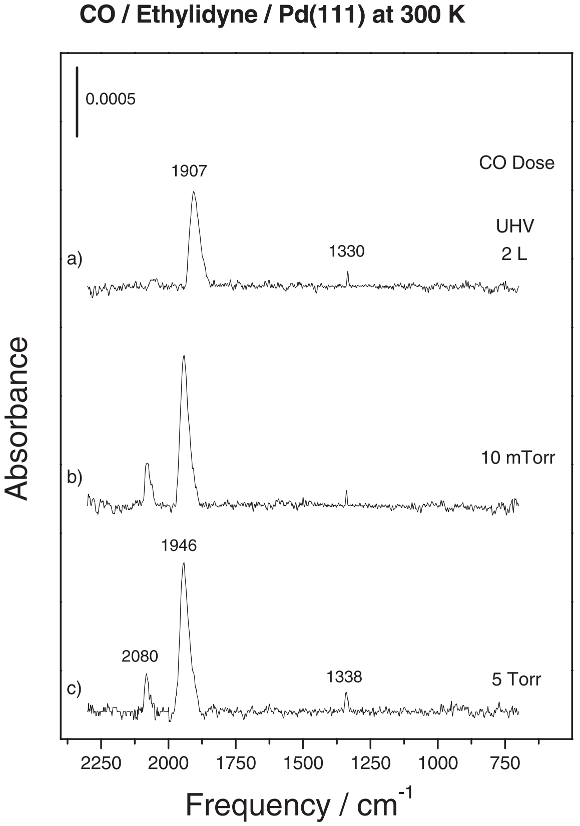

Fig. 4. RAIRS of (a) 2 L of CO on ethylidyne-covered Pd(1 1 1), (b) under a pressure of 10 mTorr of CO on ethylidyne-covered Pd(1 1 1) and (c) under a pressure of 5 Torr of CO.

4. Discussion

Ethylidyne species adsorbed on Pd(1 1 1) thermally decompose at ~425 K yielding hydrogen (Fig. 1). Extra hydrogen deposited onto the surface desorbs at ~360 K at an exposure of 2.5 L and shifts to lower temperatures as the exposure increases suggesting that the presence of ethylidyne species lowers the hydrogen desorption temperature. No other desorbing species are detected. The ethylidyne coverage can therefore be measured from the hydrogen desorption yield by comparison with the desorption yield of a hydrogen monolayer ($\Theta_{\rm sat} =\sim 1.0$ [14]). The resulting ethylidyne uptake curve is displayed as an inset in Fig. 1 which reveals that the saturation ethylidyne coverage is 0.26 ± 0.02 monolayers, a value in good agreement with the saturation coverage for ethylidyne on Pt(1 1 1) [15], which is attained at 300 K after an ethylene exposure of ~30 L on Pd(1 1 1). The ethylidyne saturation coverage is much lower than that for vinylidene species formed from acetylene on Pd(1 1 1) ($\Theta_{\rm sat} = 1.0$ [2]). This is reflected in the uptake kinetics of CO on ethylidyne-covered Pd(1 1 1) (Fig. 2), where ~0.25 monolayers of CO can be accommodated onto this surface in ultrahigh vacuum (Fig. 2) and it contrasts the behavior of CO on vinylidene-covered Pd(1 1 1), which must be pressurized for CO to adsorb onto the surface [4]. The same effect is mirrored in the lower CO desorption yield from an ethylidyne-covered surface compared to clean Pd(1 1 1) (Fig. 3). These results immediately suggest that an adsorbed ethylidyne species directly block the adsorption of CO on the surface. The adsorption sites of CO on Pd(1 1 1) have recently been re-interpreted to suggest that, at a 0.5 monolayer coverage (when CO exhibits a c(4 × 2) LEED pattern), CO occupies both face-centered cubic (f.c.c.) and hexagonal-close-packed (h.c.p.) threefold hollow sites [16], while at lower coverages (0.33 monolayers, when it exhibits a $\sqrt{3} \times \sqrt{3}\,R30°$ LEED pattern), it occupies exclusively f.c.c. hollow sites [16,17]. The proposed structures for CO on clean Pd(1 1 1) are displayed in Fig. 5(b) and (c). Recent density-functional calculations [8] corroborated this view by showing that the hollow-sites were most stable where the heat of adsorption in the $\sqrt{3} \times \sqrt{3}\,R30°$ structure was calculated to be 2.01 eV, compared to 1.85 eV for the c(4 × 2) structure [8]. That work also computed the vibrational frequencies for CO adsorbed in the f.c.c. hollow site in the $\sqrt{3}$ structure

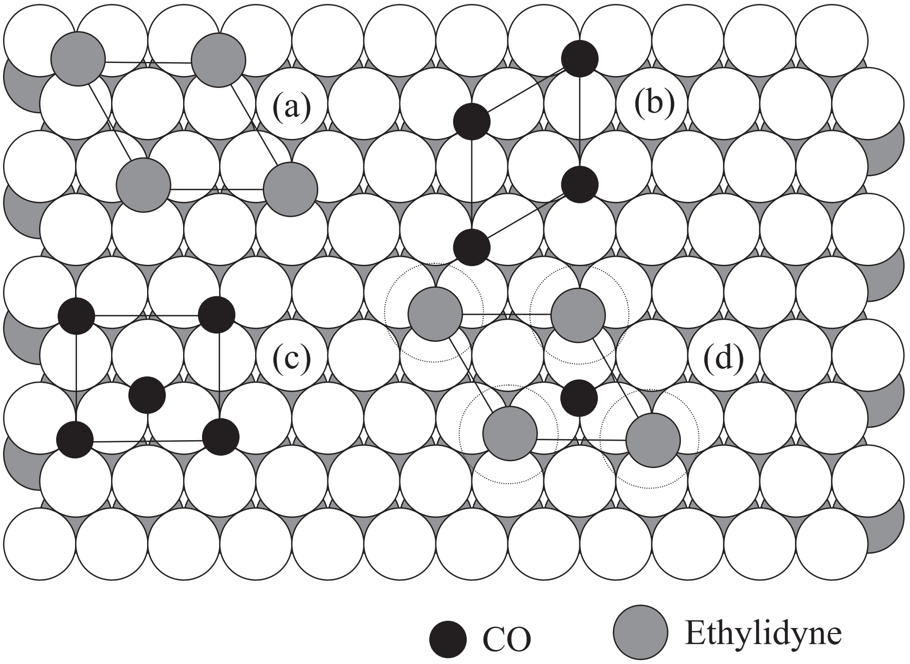

Fig. 5. Structures of (a) p(2 × 2) ethylidyne on Pt(1 1 1) [15], (b) $\sqrt{3} \times \sqrt{3}\,R30°$ CO on Pd(1 1 1) [16,17], (c) c(4 × 2) CO structure on Pd(1 1 1) [16] and (d) proposed structure for CO adsorbed on ethylidyne-covered Pd(1 1 1).

to be 1828 cm^{-1}, in good agreement with the value of 1836 cm^{-1} found experimentally [18]. The CO stretching frequency for CO in the $c(4 \times 2)$ was calculated to be 1906 cm^{-1}, where the shift was ascribed to a combination of chemical and dipole–dipole coupling interactions between the two CO molecules adsorbed in the h.c.p. and f.c.c. hollow sites in this structure [8]. The absence of any features at ~1830 cm^{-1} in Fig. 4(a) for 0.25 monolayers of CO on ethylidyne-covered Pd(1 1 1) suggests, on the basis of these calculations, that the f.c.c. sites are not occupied and thus presumably blocked by ethylidyne.

The above calculations for CO on Pd(1 1 1) [8], which found a higher heat of adsorption for CO in the $\sqrt{3}$ structure than in the $c(4 \times 2)$ structure, suggest an interpretation for the CO desorption spectrum for CO on clean Pd(1 1 1) (Fig. 3(a)). The low-temperature (360 K) state is due to desorption from the more weakly held CO in the $c(4 \times 2)$ structure. As the coverage decreases to 0.33 monolayers, CO occupies exclusively more stable f.c.c. sites and this desorbs at a higher temperature. Note that two interconverting adsorption sites were implied from molecular beam experiments [19]. This suggests that the amount of CO desorbing in the high-temperature (460 K) state should be twice that desorbing in the low-temperature (360 K) state, as found experimentally (Fig. 3(a)). The preferential attenuation of the 460 K state compared to the 360 K state on an ethylidyne-covered surface (Fig. 3) is in accord with the view that the more stable f.c.c. sites are blocked by ethylidyne. This model would suggest that the high-temperature state should be completely suppressed. Note, however, that ethylidyne decomposition is underway at ~420 K. This may allow some of the f.c.c. sites to become occupied as the ethylidyne decomposes.

LEED I/V calculations of the $p(2 \times 2)$ ethylidyne structure on Pt(1 1 1) [15] have proposed that this adsorbs at the f.c.c. site and the resulting structure shown in Fig. 5(a). A proposed CO + ethylidyne/Pd(1 1 1) structure is displayed in Fig. 5(d) assuming that ethylidyne species occupy the same f.c.c. site on Pd(1 1 1), and that CO adsorbs on the h.c.p. site as suggested above. It would, at first sight, appear that the f.c.c. site should be relatively accessible and, since it is the most stable on the clean surface [8], be preferentially occupied. However, dotted lines are shown around each ethylidyne in the structure in Fig. 5(d) representing the Van der Waals' radii of methyl species (~2 Å [20]). This reveals that the f.c.c. site is more sterically hindered by the ethylidyne species than the h.c.p. site.

CO adsorbed at this site exhibits a stretching frequency of ~1907 cm^{-1} (Fig. 4(a)), in the same range as that for the $c(4 \times 2)$ structure (1906 [17] to 1936 [18] cm^{-1}). This frequency has been suggested to be both due to bonding and dipole–dipole coupling interactions between adsorbed CO molecules [8], and assigned to the in-phase stretching mode of the two CO molecules in the unit cell. The frequency of the out-of-phase mode was calculated to be ~1850 cm^{-1}, but is infrared invisible. Based on the above discussions, the 1907 cm^{-1} feature is assigned to CO adsorbed in the h.c.p. site, where its bonding may be affected by the adjacent ethylidyne species.

When the sample is pressurized to 10^{-2} Torr, the 1907 cm^{-1} feature shifts to 1940 cm^{-1} and a feature grows at 2080 cm^{-1}. CO stretching modes between 2097 and 2110 cm^{-1} on clean Pd(1 1 1) have been assigned to CO adsorbed in the atop site [7] and Fig. 5(d) shows that this site is available for adsorption. Further pressurizing to 5 Torr causes the frequency to shift slightly to 1946 cm^{-1} and the intensity of the 2080 cm^{-1} mode remains constant. This implies that the CO coverage has reached its maximum by ~10^{-2} Torr. The increased intensity of the 1907 cm^{-1} mode (Fig. 4(b)) could imply an increased occupancy of the h.c.p. site when the surface is pressurized. However, the saturation CO coverage of ~0.25 monolayers in the presence of ethylidyne-covered Pd(1 1 1) (Fig. 2) implies that all of the h.c.p. sites are occupied following a 2 L CO exposure. A more likely explanation is that the CO in the h.c.p. and atop sites couple with the in-phase mode having a vibrational frequency of 1940 cm^{-1} and the out-of-phase combination a vibrational frequency of 2080 cm^{-1}. Such a coupling should lead to a decrease in the frequency of the "isolated" h.c.p. CO from 1907 cm^{-1} so that an additional shift must arise from a chemical interaction between the CO molecules adsorbed at these adjacent sites.

5. Conclusions

CO is proposed to adsorb on the h.c.p. hollow site following a 2 L exposure on ethylidyne-covered Pd(1 1 1). This model accounts for the saturation CO coverage on the ethylidyne-covered surface as well as the temperature-programmed desorption data. It is also in accord with the vibrational results. The f.c.c. sites, while more stable on clean Pd(1 1 1), cannot be accesses because of steric hindrance by the ethylidyne species. These results also suggest that the stable site for ethylidyne on Pd(1 1 1) is identical to that on Pt(1 1 1), occupying f.c.c. threefold hollow sites. Pressurizing the surface with 10 mTorr of CO populates the atop site, with no additional adsorption being found when the ethylidyne-covered surface is pressurized to 5 Torr.

Acknowledgements

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