Two Adsorption States of C_2H_4 at Saturation Coverage on Pd(110)-(2x1)-H

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The adsorption of C_2H_4 on Pd(110)-(2x1)-H at 160 K was studied by scanning tunneling microscopy and high-resolution electron energy loss spectroscopy. We found that two adsorbed species coexist at high coverage. The species were characterized by C-C stretching energies of 170 and 153 meV, which were identified as one-dimensional and c(2x2) domains, respectively. The latter species, which appeared only at high coverage, was bonded to the bare surface, which implied the possibility of H atom transition into the subsurface.

Palladium is known as a good catalyst for the hydrogenation reaction. The coadsorption states of ethylene with hydrogen on low-Mirror-index surfaces have been studied to elucidate the reaction mechanism.[1-3]

Adsorbed H atoms occupy quasi-threefold-coordinated sites on Pd(110)[4,5] and form a (2x1) structure at 1 ML (1 ML corresponds to the number of metal atoms on a bulk metal surface).[6,7] Ethylene molecules occupy on-top sites on a 1 ML (2x1)-H surface with π-bonding character below 260 K.[1] Thus, site blocking due to the preadsorbed H does not occur for C_2H_4 adsorption.[1] We recently reported that the symmetry of low-coverage C_2H_4 was markedly changed by coadsorbed H.[2]

A previous study at higher coverage revealed a weakly bonded C_2H_4 which desorbed intact at ~ 150 K.[1] In this letter, we report the adsorption states of high-coverage C_2H_4 at 160 K on (2x1)-H/Pd(110) studied using high-resolution electron energy loss spectroscopy (HREELS) and scanning tunneling microscopy (STM) in which two different adsorbed species were found.

The experiments for STM and HREELS were performed separately. The former were carried out in an ultrahigh vacuum system (< 1 x 10^{-10} Torr) equipped with a three-grid retarding field analyzer for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), a quadrupole mass spectrometer and a Beetle STM (Besocke Delta Phi GmbH).[8] A Pd crystal was mounted on a "triple helix" sample holder.[8] The sample was heated by electron bombardment from the rear and was cooled to ~ 100 K by contact with a Cu arm attached to a liquid N_2 reservoir.

The ultrahigh vacuum system[9] for HREELS experiments was also equipped with an apparatus similar to that of the STM system. We used a HREELS (VSI; DELTA 0.5) with a typical energy resolution of 3 meV. In this work, scattered electrons were detected in the specular direction with the scattering azimuth along [1$\bar{1}$0]. The HREELS measurements were conducted at 85 K.

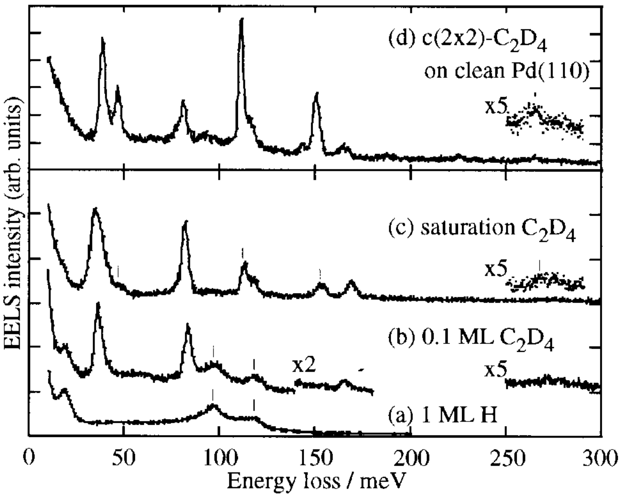

Figure 1. HREELS spectra for (a) 1 ML (2x1)-H surface; (b) low-coverage C_2D_4 on the (2x1)-H surface; (c) saturation C_2D_4 at 160 K on the (2x1)-H surface, and (d) c(2x2) C_2D_4 on the clean Pd(110) surface.

Table 1. Observed vibrational energies of C_2D_4 on Pd(110) and Pd(110)-(2x1)-H in units of meV[a]

Mode		Pd(110)-(2x1)-H		Pd(110)
		[b]low θ_{C2D4}	high θ_{C2D4} two species	high θ_{C2D4}
C-H stretch	a1	272	275/268	265
C-C stretch	a1	166	170/153	151
scissors	a1	118	118	116
wagging	b1	-	- /113	112
	a1	84	82	81
Pd-C	b1	-	- / 48	47
	a1	37	35	38

[a]For reference, those for low-coverage C_2D_4on the both surfaces are also shown.
[b]Reference 2

A clean Pd(110) surface was prepared by normal procedures and confirmed by HREELS, LEED and STM.[10] The (2x1)-H/Pd(110) was prepared by introducing H_2 gas on a clean surface, which gives rise to the dissociative adsorption of H atoms to form a (2x1) structure at 1.0 ML.[6,7] The (2x1)-H structure and the coverage were confirmed by LEED and thermal desorption spectroscopy (TDS), respectively.

Figure 1a shows an HREELS spectrum for a Pd(110)-(2x1)-H surface. Hydrogen-derived loss peaks appear at 98 and 120 meV.[11] Figure 1b shows an HREELS spectrum for low-coverage (0.1 ML) C_2D_4 on a (2x1)-H surface. The loss peaks were previously assigned[2] and are summarized in Table 1. Figure 1c shows an HREELS spectrum of a (2x1)-H surface saturated with C_2D_4 at 135 K and subsequently annealed to 160

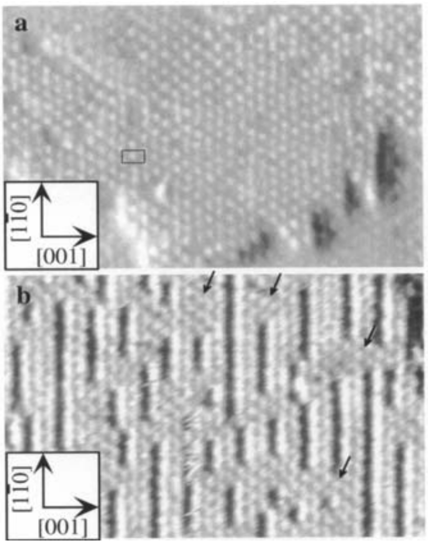

Figure 2. (a) An STM image of c(2x2)-C_2H_4 on the clean Pd(110) surface. Area = 150 x 100 A^2. Tip bias E_t = - 0.06 V and tunneling current I_t = 1.5 nA. (b) An STM image of the (2x1)-H surface saturated with C_2H_4 at 160 K. Area = 150 x 100 A^2. E_t = -0.05V and I_t = 0.6 nA. Some c(2x2) domains are indicated by arrows.

K. The spectrum is also similar to one shown in the previous work.[1] New peaks at 48, 113, 153 and 268 meV also appeared in addition to those observed at low coverage. The energies of the additional peaks are similar to those for C_2D_4 on a clean Pd(110) surface, as mentioned below.

Figure 1d shows a spectrum of 0.5 ML C_2D_4 on a clean Pd(110) surface with a c(2x2) structure.[12] The comparison between Figure 1c and Figure 1d indicates that the peak at 153 meV in Figure 1c corresponds to the C-C stretching mode ($\nu_{c\text{-}c}$) at 151 meV in Figure 1d. The other three peaks at 48, 113 and 268 meV, which appeared at high coverage on the H-covered surface, also correspond to those observed on the clean Pd(110) surface. The assignments of these peaks are also summarized in Table 1.[2] Two kinds of C_2D_4 characterized by $\nu_{c\text{-}c}$ at 170 and 153 meV are revealed. These results indicate that the second species observed only at high coverage is bonded to bare Pd(110) although the surface was fully covered with H atoms.

Figure 2a shows an STM image of 0.5 ML C_2H_4 on clean Pd(110), where the surface is exposed to C_2H_4 gas at 110 K and observed at 250 K. The c(2x2) structure almost covers the Pd(110) surface, which agrees with the LEED results.[12] Figure 2b shows an STM image of the (2x1)-H surface saturated with C_2H_4 at 160 K and observed at 141 K. The coverage of C_2H_4 was 0.40 ML at 160 K. The adsorption structures were quite different in Figures 2a and 2b. On the H-covered surface, C_2H_4 formed a characteristic one-dimensional chain along [1$\bar{1}$0]. The chains were missing every third row, giving rise to the paired structure. They have an average length of about eight Pd atoms along [1$\bar{1}$0]. This paired structure is characteristic of the adsorption of C_2H_4 on H-covered surface and thus corresponds to the first species observed by HREELS ($\nu_{c\text{-}c}$ = 170 meV). On the other hand, at the domain boundary of these one-dimensional structures, another domain with a local c(2x2) structure was found to coexist, which is presumably associated with the second species ($\nu_{c\text{-}c}$ = 153 meV). Its local c(2x2) structure implies adsorption on a bare surface, which is in good agreement with the HREELS results.

We now discuss the mechanism of C_2H_4 adsorption on the H-covered Pd(110). As the coverage increased, both HREELS and STM revealed a second species on (2x1)-H/Pd(110), which was ascribed to C_2H_4 adsorbed on a bare surface. This indicates that the postadsorption of C_2H_4 induced the removal of H atoms from the surface; we suggest the process of H atom transition to subsurface sites, although the possibility of desorption cannot be ruled out. This process is supported as follows: (i) The activation energy of bulk absorption of H atoms from a surface site is at most 0.58 eV, while that of desorption is 0.87 eV.[6] (ii) In previously reported TDS results for this system,[1] the desorption peak of H_2 has a shoulder at ~ 250 K, where the presence of H atoms in the subsurface has been suggested. (iii) The transition of adsorbed H atoms into the subsurface caused by coadsorption was also observed for the CO/H/Pd(100) system.[13]

The STM and HREELS studies reported herein clearly proved the presence of two C_2H_4 species on Pd(110)-(2x1)-H surface. The species were characterized by C-C stretching energies of 170 and 153 meV, which were identified by STM as one-dimensional and c(2x2) domains, respectively. We suggest that the latter species, which appeared only at high coverage, is bonded to the bare surface formed by the transition of preadsorbed H into subsurface sites.

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