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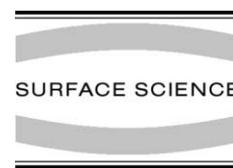
Surface Science Letters

The adsorption of ethylene on ethylidyne-covered Pd(1 1 1)

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Abstract

Reflection absorption infrared spectroscopy shows that ethylene adsorbs on ethylidyne-saturated Pd(1 1 1) ($\Theta_{sat}(CH_3-C\equiv) = 0.25$) at 80 K exhibiting a feature at 1100 cm^{-1}, assigned to di-σ-bonded ethylene adsorbed on the palladium surface. Since adsorbed ethylidyne also has a vibrational mode at $\sim$1090 cm^{-1}, the assignment of the 1100 cm^{-1} mode to adsorbed ethylene was confirmed by adsorbing it on an ethylidyne-covered surface grown using deuterated ethylene. The adsorption of ethylene on ethylidyne-covered Pd(1 1 1) was further confirmed using temperature-programmed desorption which revealed that the saturation ethylene coverage on ethylidyne-covered Pd(1 1 1) is 0.25 compared to 0.33 for ethylene on clean Pd(1 1 1).
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1. Introduction

The adsorption of ethylene has been extensively studied on noble metal surfaces since these catalyze the hydrogenation of unsaturated carbon–carbon bonds [1]. Ethylene adsorbs molecularly at low temperatures (<250 K) but converts to a more strongly bound ethylidyne species ($CH_3-C\equiv$) at higher temperatures ($\sim$300 K) [2,3]. This species covers the surface during ethylene hydrogenation but is removed by high pressures of hydrogen [4]. It has been suggested, based on estimates of the van der Waals' contours of ethylene and ethyli-

dyne, that ethylene cannot adsorb onto an ethylidyne-covered Pt(1 1 1) surface, leading to an early proposal that the role of the ethylidyne species in ethylene hydrogenation was to transfer surface atomic hydrogen to ethylene adsorbed in the second layer [5]. Subsequently, both theoretical [6] and experimental [7,8] results have supported the stepwise addition of atomic hydrogen to adsorbed ethylene according to the so-called Horiuti–Polanyi mechanism [9]. It has further been demonstrated using sum-frequency generation (SFG) on Pt(1 1 1) that, under high-pressure conditions at 300 K, both π- and di-σ-bonded species are present on the surface in the presence of ethylidyne species, but that the presence of ethylidyne considerably suppresses the adsorption of di-σ-bonded ethylene [10]. It is however demonstrated in the following, using both infrared spectroscopy

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and temperature-programmed desorption, that a significant coverage of di-σ-bonded ethylene adsorbs onto an ethylidyne-saturated Pd(1 1 1) surface ($\Theta_{sat}(CH_3-C\equiv) = 0.25$) at 80 K in ultrahigh vacuum.

2. Experimental

Infrared and temperature-programmed desorption data were collected using systems that have been described previously [11,12]. The Pd(1 1 1) sample was cleaned using a standard procedure which consisted 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, and the absence of surface carbon established using temperature-programmed desorption as described previously [11].

Ethylene (Matheson) was transferred to glass bottles and attached to the gas-handling systems of the vacuum chambers and further purified by
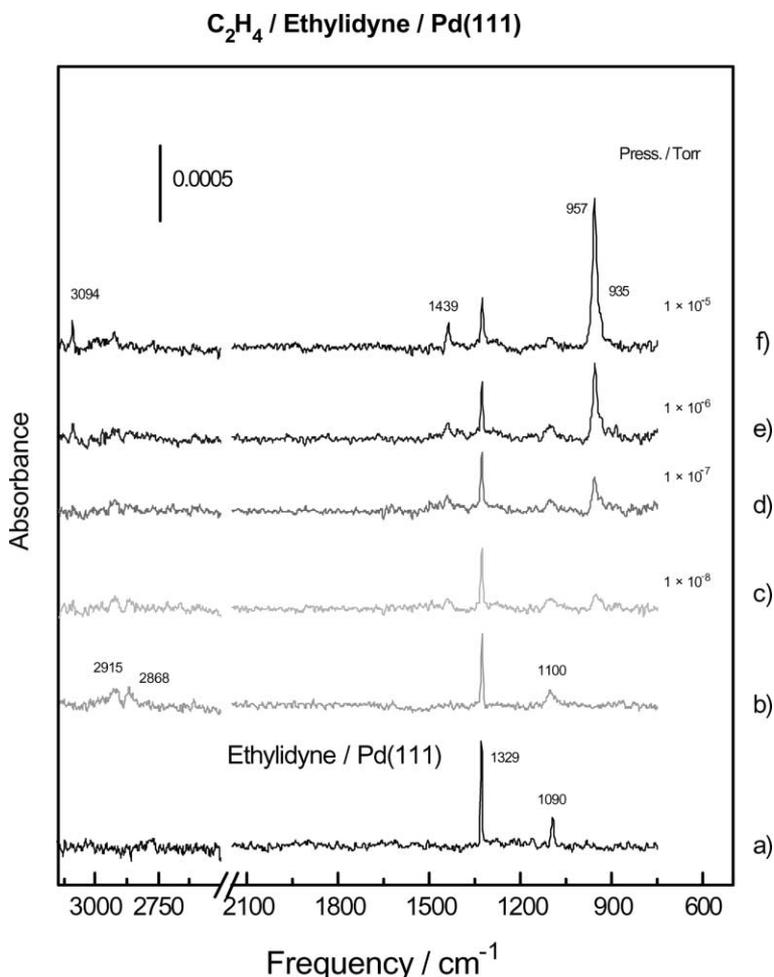

Fig. 1. Reflection absorption infrared spectra of (a) ethylidyne formed on Pd(1 1 1) by exposing the sample to 30 L of ethylene at a sample temperature of 350 K (Θ(ethylidyne) = 0.25) and (b) ethylidyne-covered surface exposed to 10 L of ethylene at 80 K. Spectra (c–f) show the effect of pressurizing the surface with ethylene at a sample temperature of 80 K where the ethylene pressures are (c) 1×10^{-8} Torr, (d) 1×10^{-7} Torr, (e) 1×10^{-6} Torr and (f) 1×10^{-5} Torr.

several freeze–pump–thaw cycles. C_2D_4 (Cambridge Isotopes, 98% D) and deuterium (Linde, CP Grade) were used as received. The cleanliness of all reactants was monitored by mass spectroscopy.

3. Results and discussion

As noted above, the catalytic hydrogenation of ethylene on Pd(1 1 1) takes place on an ethylidyne-covered surface so that, from a catalytic point of view, it is of interest to explore whether ethylene can adsorb on this surface [5,10,13]. The reflection absorption infrared spectra (RAIRS) for ethylene adsorbed on ethylidyne-saturated Pd(1 1 1) are displayed in Fig. 1, where Fig. 1(a) shows the infrared spectrum of ethylidyne formed by exposing Pd(1 1 1) to 30 L of ethylene at 350 K. This displays its characteristic features at 1329 and 1090 cm^{-1}, assigned to the CH_3 bending and C–C stretching modes respectively [11]. Fig. 1(b) shows the spectrum collected following ethylene
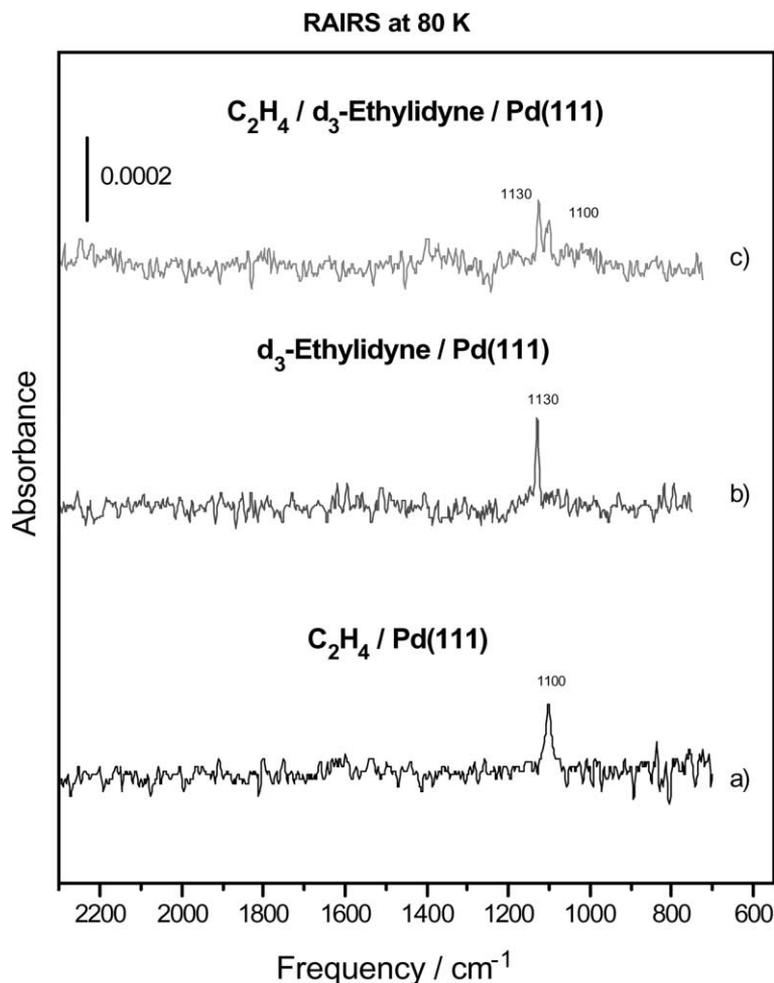

Fig. 2. Reflection absorption infrared spectra of (a) 10 L of ethylene adsorbed on clean Pd(1 1 1) at 80 K, (b) d_3-ethylidyne formed on Pd(1 1 1) by exposing to 30 L of d_4-ethylene at a sample temperature of 350 K and (c) after exposure of the d_3-ethylidyne-covered surface to 10 L of C_2H_4.

adsorption (10 L) on ethylidyne-covered Pd(1 1 1) at 80 K. The 1329 cm^{-1} feature is slightly attenuated in intensity and the peak absorbance is ~65% of that on clean Pd(1 1 1). A broad feature is present at ~1100 cm^{-1}. This feature is much broader than the 1090 cm^{-1} ethylidyne feature and is assigned to the presence of a combination of the 1090 cm^{-1} ethylidyne C–C stretching mode and a 1100 cm^{-1} di-σ-bonded ethylene peak [14]. No features are detected at ~940 cm^{-1} indicating the absence of any π-bonded species on an ethylidyne-covered surface [14]. Fig. 1(c–f) documents the effect of pressurizing the sample with ethylene. The peak absorbance of the 1329 cm^{-1} ethylidyne mode continues to decrease slightly. Most striking, however, is the appearance of an intense 957 cm^{-1} feature also found previously on ethylene- and CO-covered Pd(1 1 1) [14]. This feature also displays a shoulder at 935 cm^{-1} with a peak at 1439 cm^{-1}, and the corresponding C–H stretching mode is detected at 3094 cm^{-1}. However, these features have been assigned to ethylene adsorbed in second and subsequent layers on Pd(1 1 1) [14]. A similar intense feature was observed after pressurizing Pt(1 1 1) with ethylene and, in this case, was assigned to π-bonded ethylene [13].

Since the feature at ~1100 cm^{-1} observed following ethylene adsorption on ethylidyne-covered Pd(1 1 1) is close to the ethylidyne C–C stretching mode at 1090 cm^{-1} [11], ethylene was adsorbed on an ethylidyne-covered surface prepared using C$_2$D$_4$. The results of this experiment are displayed in Fig. 2. Fig. 2(a) shows the spectrum for ethylene on clean Pd(1 1 1) for comparison, and Fig. 2(b) displays the spectrum for d_3-ethylidyne on Pd(1 1 1) which exhibits a feature at 1130 cm^{-1}, assigned to the C–C stretching mode, in good agreement with the value found for an ethylidyne-containing organometallic [15], and for d_3-ethylidyne on Pt(1 1 1) [16]. These frequencies are now sufficiently different that any ethylene adsorbed on the ethylidyne-covered surface will be easily distinguishable from the ethylidyne features. This is illustrated in spectrum 2(c) which exhibits both the 1130 cm^{-1} ethylidyne feature and the 1100 cm^{-1} ethylene mode. This confirms that ethylene adsorbs in ultrahigh vacuum on ethylidyne-saturated Pd(1 1 1) and that it is di-σ-bonded on this surface.

TPD of Ethylene adsorbed at 150 K
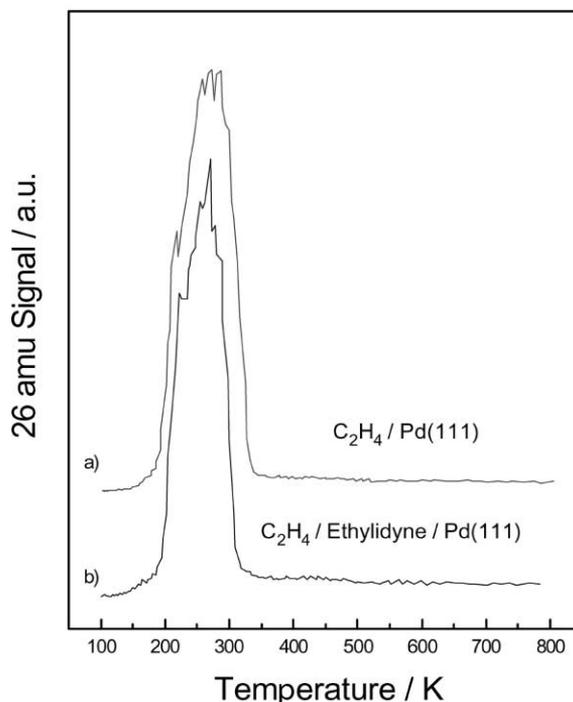
Fig. 3. Temperature-programmed desorption spectrum of ethylene (10 L) adsorbed on (a) clean Pd(1 1 1) and on (b) ethylidyne-covered Pd(1 1 1) at 150 K monitoring 26 amu (ethylene).

Furthermore, the ethylidyne overlayer has no effect on the state of ethylene hybridization which is identical to that found on clean Pd(1 1 1) (Fig. 2(a) [14]).

The presence of ethylene on ethylidyne-saturated Pd(1 1 1) is further confirmed by the temperature-programmed desorption data shown in Fig. 3. Spectrum 3(a) shows results for 10 L of ethylene adsorbed on clean Pd(1 1 1) and spectrum 3(b) is that for ethylene on an ethylidyne-saturated surface. The 26 amu spectra clearly show that ethylene adsorbs on ethylidyne-covered Pd(1 1 1) in accord with the infrared data of Figs. 1 and 2. Comparing the areas under the ethylene temperature-programmed desorption spectra in Fig. 3(a) and (b) and using the saturation coverage of ethylene on Pd(1 1 1) ($\Theta_{sat} = 0.33 \pm 0.03$ [17,18]) yields an ethylene coverage on ethylidyne-saturated Pd(1 1 1) of 0.25 ± 0.05 monolayers (where in

all cases coverages are referenced to the palladium atom density on the (1 1 1) surface).

These results show that ethylene can adsorb onto ethylidyne-saturated Pd(1 1 1) and that the ethylene saturation coverage is only slightly affected by the presence of an ethylidyne overlayer. In this case, the ethylene is di-σ-bonded, identical to that found on clean Pd(1 1 1) [14] indicating that the presence of an ethylidyne overlayer has no effect of the state of adsorbed ethylene. It was found, however, that the presence of a hydrogen overlayer on Pd(1 1 1) did have a substantial effect since, in this case, ethylene is π-bonded on the surface [14]. The saturation ethylene coverage is identical to that of the ethylidyne species, consistent with ethylene adsorbing in the sites available between the ethylidynes in the saturated overlayer and is also consistent with the adsorption of CO on ethylidyne-saturated Pd(1 1 1) where two CO molecules were proposed to adsorb in this space as the pressure increases [19].

Acknowledgements

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