

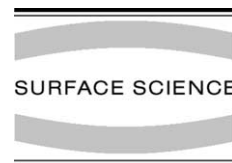


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# Structure and reactivity of propylene on clean and hydrogen-covered Pd(1 1 1)

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## Abstract

The adsorption of propylene on clean and hydrogen-covered Pd(1 1 1) has been studied by using temperature-programmed desorption (TPD) and reflection-absorption infrared spectroscopy. Propylene adsorbs in a di- $\sigma$  configuration on clean Pd(1 1 1). At high exposures, it forms second and subsequent layers. Upon heating, propylene desorbs molecularly at  $\sim 200$  and 280 K and, in contrast to ethylene adsorbed on Pd(1 1 1), it undergoes significant dehydrogenation. Two major products of dehydrogenation were identified: propylidyne and  $\eta^1$ -allyl species. While the formation of  $\eta^1$ -allyl species was found to be favored, both are observed to co-exist on the surface. The pre-adsorption of hydrogen induces the appearance of some  $\pi$ -bonded propylene. The conversion to this weaker state of adsorption induced by hydrogen is not complete, due to steric effects caused by the methyl group. Formation of propane is observed by reaction of hydrogen with propylene in TPD experiments, and the activation energy is measured to be  $3.4 \pm 0.4$  kcal/mol.

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## 1. Introduction

Although an apparently rather simple reaction, the details of the mechanisms of transition-metal-catalyzed hydrogenation reactions are still not fully understood. The general reaction pathway, first proposed by Horiuti and Polanyi [1], envisages a sequential addition of atomic hydrogen across the double or triple bond of the alkene or

alkyne respectively. It has since been found on (1 1 1) surfaces of group VIII metals that reaction does not proceed on a clean metal surface, but one that is covered by strongly bound carbonaceous species, like ethylidyne in the case of ethylene hydrogenation [2]. It has been suggested previously that these strongly bound species effectively prevent molecular adsorption onto the metal surface, but it has recently been demonstrated that ethylene can adsorb onto ethylidyne-covered Pd(1 1 1) in ultra-high vacuum and thus the ethylidyne apparently acts as a spectator species during ethylene hydrogenation [3]. It has been shown, using reflection-absorption infrared spectroscopy (RAIRS), that

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ethylene is rehybridized when chemisorbed on clean Pd(111), but to a lesser extent than on Ni and Pt(111) [4]. However, adsorbing ethylene onto hydrogen-covered Pd(111) leads to the formation of  $\pi$ -bonded ethylene. The presence of hydrogen on the surface therefore has a profound effect on the ethylene adsorption state [4]. It has been suggested that more weakly bound  $\pi$ -bonded species are more readily hydrogenated than the di- $\sigma$  form, so that such a change in hybridization in the presence of co-adsorbed hydrogen would have an effect on the catalytic hydrogenation kinetics. There have been substantially fewer investigations of propylene than ethylene on group VIII transition-metal surfaces with the most complete investigations being carried out on Pt(111). In this case, two distinct di- $\sigma$ -bonded species were found at 80 K as well as the formation of a  $\pi$ -bonded second layer [5,6]. The formation of propylidyne species, analogous to the ethylidyne species formed from ethylene, was found at higher temperatures. Propylidyne has been formed and characterized previously by adsorbing propylene on Pt(111) at room temperature [7]. The nature of a Pt(111) surface has been probed under reaction conditions by second-harmonic generation, where  $\pi$ - and di- $\sigma$ -bonded propylene, propylidyne, 2-propyl and vinyl methylidyne species were suggested to co-exist [8].

Palladium is also extensively used for the synthesis of functionalized olefins [9]. It is therefore of interest to explore the mechanism of olefin dehydrogenation. In particular, coupling reactions between organometallic nucleophiles and organo halide electrophiles on Pd complexes are well known and have been successfully implemented for over 20 years [10]. The key step in such reactions is the formation of a  $\pi$ -allyl complex at the metal center from an olefinic reactant. The nucleophilic attack may then take place at a terminal or central carbon. While a general outline of the mechanism has been proposed [9], the details of individual steps remain less well understood.

A previous kinetic study of propylene on Pd(111) has been performed using laser induced thermal desorption (LITD), where only one chemisorbed state was found in addition to a condensed layer [11]. In view of the differences

between the chemistry of ethylene on Pd(111) and Pt(111), particularly regarding the effect of hydrogen on the state of ethylene hybridization on Pd(111), and to try to further understand the interaction of olefinic molecules with palladium, the chemistry of propylene on Pd(111) is investigated in the following.

## 2. Experimental

Infrared data were collected using a system that has been described previously [12]. Briefly, a palladium single crystal was mounted in a modified  $2\frac{3}{4}$  six-way cross equipped with infrared-transparent, KBr windows. It could be resistively heated to 1200 K, or cooled to 80 K using liquid nitrogen. Infrared spectra were collected using a Bruker Equinox infrared spectrometer and a liquid-nitrogen-cooled, mercury cadmium telluride detector. The complete light path was enclosed and purged with dry, CO<sub>2</sub>-free air. Data were typically collected for 1000 scans at 4 cm<sup>-1</sup> resolution.

Temperature-programmed desorption (TPD) data were collected in another ultrahigh vacuum chamber that has been described in detail elsewhere [13] where desorbing species were detected using a Dycor quadrupole mass spectrometer placed in line of sight of the crystal.

The Pd(111) sample was cleaned using a standard procedure that 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. Since the carbon KLL Auger feature is effectively obscured by a strong palladium peak, Auger spectroscopy is insensitive to the presence of small amounts of surface carbon. A more sensitive gauge of carbon coverage was to saturate the surface with oxygen and perform a TPD 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. The complete absence of carbon is indicated by the desorption of only O<sub>2</sub>.

Propylene (Aldrich, >99%), hydrogen (Matheson, Research Grade) and deuterium (Linde, CP

Grade) were transferred to glass bottles, which were attached to the gas-handling systems of the vacuum chambers. Propylene was further purified by several freeze–pump–thaw cycles. The cleanliness of all reactants was monitored mass spectroscopically.

### 3. Results

#### 3.1. Adsorption of propylene on Pd(111) at low temperature

Predominantly hydrogen and propylene desorption are found following the adsorption of propylene on Pd(111). Propylene (41 amu) temperature-desorption data are displayed in Fig. 1 as a function of propylene exposure (exposures were not corrected for ion gauge sensitivities). The desorption profile for low propylene exposures exhibits a broad feature centered at  $\sim 210$  K, which grows and shifts to  $\sim 195$  K with increasing exposure. A small additional feature becomes evident at  $\sim 340$  K following an exposure of 1.1 L of propylene, which grows slightly with increasing exposure, but remains rather small. A third state appears at  $\sim 280$  K for exposures greater than 1.3 L, which shifts to lower temperatures with increasing exposure and appears at  $\sim 260$  K after an exposure of 4 L (corresponding to propylene saturation). Finally, a sharp feature is evident at  $\sim 190$  K for exposures larger than 1.5 L, which saturates following an exposure of  $\sim 4$  L of propylene. An additional small desorption state appears at 110 K and continues to grow with increasing exposure. The vapor pressure of propylene at 80 K is  $\sim 2.6 \times 10^{-8}$  Torr [14] so that no multilayer condensation is to be expected at a sample temperature of 80 K when the background pressure is  $\sim 1 \times 10^{-10}$  Torr. A propylene desorption state, which appears at higher exposures ( $>1$  L) on Pt(111) at  $\sim 180$  K, has been assigned to undistorted propylene adsorbing in the second layer [5]. Similar second-layer adsorption of undistorted ethylene has been found on Pd(111) [4] where multilayer condensation is even more unlikely since the vapor pressure of ethylene at 80 K is  $\sim 1.9 \times 10^{-3}$  Torr [15]. This suggests that the

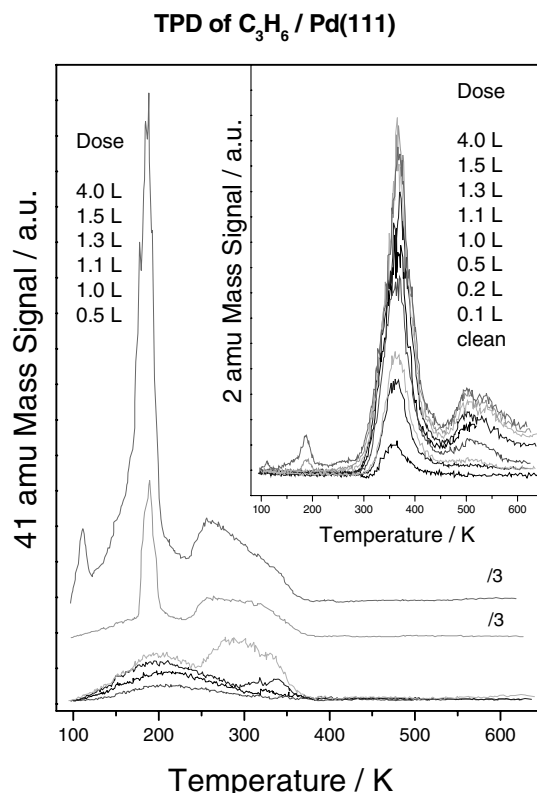


Fig. 1. TPD spectra of propylene (41 amu) adsorbed on Pd(111) at 80 K as a function of propylene exposure. Propylene exposures are marked adjacent to the corresponding spectrum. The inset shows the corresponding hydrogen (2 amu) TPD spectra.

sharp, 190 K desorption state found on Pd(111) is similarly due to the adsorption of propylene into the second layer and the one at 110 K to adsorption into a subsequent layer. The corresponding hydrogen (2 amu) desorption data are displayed in Fig. 1 (inset). A peak at 360 K, a temperature slightly higher than that at which molecular hydrogen desorbs from a clean surface, is observed starting at low exposures, which grows and saturates at  $\sim 1$  L exposure. A second peak develops at  $\sim 500$  K for exposures greater than 0.5 L. High-temperature hydrogen desorption peaks are usually associated with the decomposition of hydrocarbon species strongly bound to the metal surface. Finally, a low temperature peak develops at  $\sim 190$  K at the same exposure at which

multilayer desorption is observed (Fig. 1), which is assigned to fragmentation of the second-layer propylene desorption state.

The corresponding reflection-absorption infrared (RAIRS) spectra are displayed in Fig. 2. At low exposures (0.5 L, Fig. 2(a)), the spectrum exhibits a sharp feature at  $1005\text{ cm}^{-1}$  with less intense features at  $\sim 920$  and  $2890\text{ cm}^{-1}$ . As the exposure increases (Fig. 2(b)–(d)), the  $1005\text{-cm}^{-1}$  peak shifts to  $1014\text{ cm}^{-1}$  and the  $2890\text{-cm}^{-1}$  feature grows somewhat in intensity, and a weak feature appears at  $1439\text{ cm}^{-1}$ . The peak at  $\sim 920\text{ cm}^{-1}$  remains reasonably constant in intensity, but evolves into two features as the coverage increases. The spectrum in Fig. 2(c) corresponds to full development of the  $\sim 200$  and  $300\text{ K}$  features in the TPD spectrum (Fig. 1). A number of additional features are evident at higher exposures (Fig. 2(d)–(e)) at  $3081$ ,  $3067$ ,  $2980$ ,  $2965$ ,  $2942$ ,  $1647$ ,  $1452$ ,

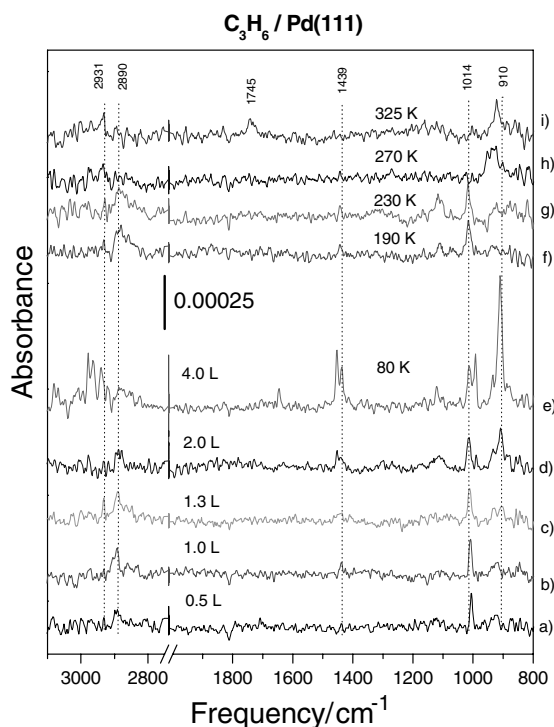


Fig. 2. Reflection-absorption infrared spectra of propylene adsorbed on Pd(111) at 80 K as a function of exposure; (a) 0.5 L, (b) 1.0 L, (c) 1.3 L, (d) 2.0 L and (e) 4.0 L and subsequently after annealing at various temperatures and allowing to cool to 80 K; (f) 190 K, (g) 230 K, (h) 270 K and (i) 325 K.

$1437$ ,  $1416$ ,  $1116$ ,  $991$ ,  $937$  and  $910\text{ cm}^{-1}$ . The appearance of these features coincides with the onset of the sharp 190 K propylene desorption state (Fig. 1). The small feature detected at  $910\text{ cm}^{-1}$  in the RAIRS spectrum following a 1.3 L propylene exposure, is assigned to the appearance of a small amount of second-layer propylene. When the Pd(111) sample is heated to 190 K, these intense features disappear restoring the spectrum with features at  $1014$ ,  $1439$  and  $2890\text{ cm}^{-1}$  plus a feature at  $1116\text{ cm}^{-1}$ . This observation confirms that the 190 K desorption state (Fig. 1) is indeed associated with the intense vibrational features that are evident in the spectra in Fig. 2(e). As the sample is heated to 230 K (Fig. 2(g)), the feature at  $1116\text{ cm}^{-1}$  remains. The spectrum changes drastically by heating to 270 K (Fig. 2(h)), yielding a broad feature centered at  $\sim 937\text{ cm}^{-1}$ . Further heating to 325 K (Fig. 2(i)) results in a further change producing features at  $937$ ,  $1745$  and  $2931\text{ cm}^{-1}$ . In contrast with the trend observed for ethylene on Pt(111) and Pd(111), where the majority of the ethylene desorbs molecularly [17], a clear indication of propylene decomposition is observed on both Pt(111) [6] and Pd(111) (Fig. 1 (inset) and Fig. 2).

### 3.2. Adsorption of propylene on a hydrogen covered Pd(111) surface

The effect of pre-dosing Pd(111) with 10 L of hydrogen and then exposing to 1.3 L of propylene is shown in Fig. 3. The 1.3 L propylene exposure was selected since it corresponds to saturation of the overlayer (assuming that the sharp 190 K peak is associated with second-layer propylene). Fig. 3 compares the desorption spectra, collected at 2 (hydrogen), 29 (propane) and 41 (propylene) amu, of a 1.3 L propylene exposure on clean Pd(111) with the same exposure on the hydrogen-covered surface. The desorption spectra for propylene on the hydrogen-covered surface are labeled A, while those on the clean surface are labeled B. Pre-dosing with hydrogen results in a significant change in the shape of the propylene (41 amu) desorption profile. The spectrum now consists of a

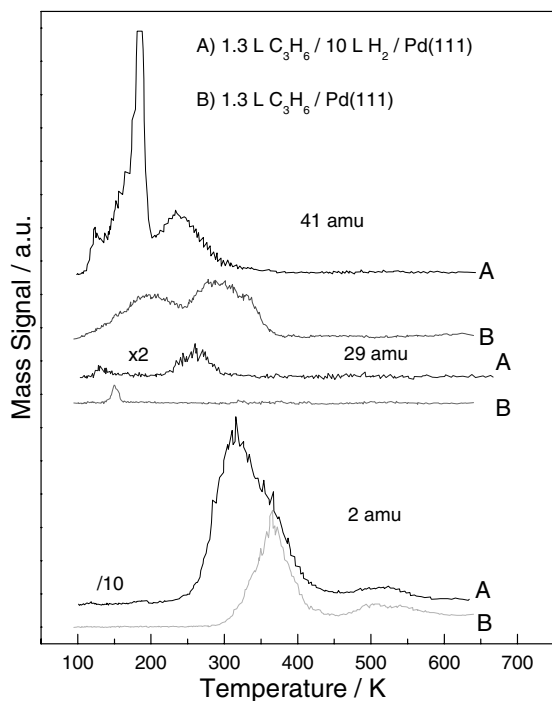


Fig. 3. TPD spectra comparing the behavior of propylene on (B) clean Pd(111) (1.3 L) with propylene adsorbed on (A) hydrogen-pre-dosed Pd(111) with a hydrogen exposure of 10 L, monitored at 41 (propylene), 29 (propane) and 2 (hydrogen) amu.

relatively symmetric feature at  $\sim 235$  K with an integrated area substantially lower than that on the clean surface, implying that propylene adsorption is blocked by the presence of hydrogen on the surface. This is in agreement with the behavior found for ethylene on Pd(111), where the ethylene adsorption is slightly affected by surface hydrogen [18]. The 190 K feature, which is only detected for exposures greater than 1.3 L on clean Pd(111), is clearly evident after an exposure of 1.3 L on the hydrogen-covered surface. 29 amu signals are detected at  $\sim 150$  K on clean Pd(111), and in a broad feature at  $\sim 260$  K on the hydrogen-covered surface. The latter feature is assigned to the hydrogenation of propylene to propane on hydrogen-covered Pd(111). The trailing edge of the  $\sim 260$  K (29 amu) feature is coincident with the trailing edge of the propylene (41 amu) desorption state, in accord with this view. TPD experiments

using pre-adsorbed deuterium were conducted by measuring 29, 30, 31, 32, 33 and 34 amu signals to study H–D exchange with adsorbed propylene, and resulted in no exchange being detected. The propane (29 amu) desorption temperature ( $\sim 260$  K) is similar to that found for ethylene hydrogenation on Pd(111) [17]. The 150 K peak in the clean-surface spectrum is unlikely to be due to propylene self-hydrogenation. A similar feature detected for propylene on clean Pt(111) has been ascribed to the desorption of propyl radicals on the basis of the mass spectrometer ionizer fragmentation pattern, and similar observations on other surfaces [6].

The corresponding RAIRS data are displayed in Fig. 4 and are different from those found on clean Pd(111). First, the peak absorbance of the features are lower than on the clean surface

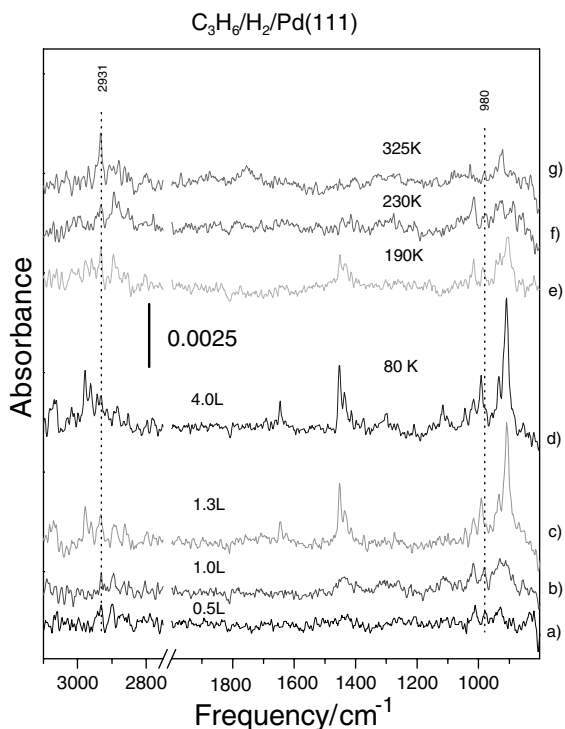


Fig. 4. Reflection-absorption infrared spectra of propylene adsorbed on hydrogen-covered Pd(111) at 80 K, with a hydrogen exposure of 10 L, as a function of propylene exposure; (a) 0.5 L, (b) 1.0 L, (c) 1.3 L and (d) 4.0 L and subsequently after annealing at various temperatures and allowing to cool to 80 K; (e) 190 K, (f) 230 K and (g) 325 K.

reflecting the lower coverage of propylene on the hydrogen-covered surface. Second, the intense features corresponding to the second-layer propylene are already clearly present at an exposure of 1.3 L (Fig. 4(c)) in accord with the TPD data where the 190 K propylene desorption state appears at lower propylene exposures (Fig. 3). In addition, the relative intensities of the infrared features on the hydrogen-covered surface are different from those on clean Pd(111) (Fig. 2). In particular, the intensities of the 1011 and 930  $\text{cm}^{-1}$  peaks (which occur at 1005 and  $\sim 920 \text{ cm}^{-1}$  respectively on the clean surface) are almost identical on the hydrogen-covered surface, while the 1005  $\text{cm}^{-1}$  mode is more intense on clean Pd(111). Two new features at 980 and 2931  $\text{cm}^{-1}$  are also detected. Thus, at low coverages (0.5 L, Fig. 4(a)), the spectrum displays peaks at 930, 980, 1011, 2900 and 2931  $\text{cm}^{-1}$  with a broad feature at  $\sim 1436 \text{ cm}^{-1}$ . The 1436  $\text{cm}^{-1}$  mode shifts to 1441  $\text{cm}^{-1}$  as the coverage increases, the 1011  $\text{cm}^{-1}$  mode shifts to 1015  $\text{cm}^{-1}$ , and the 980  $\text{cm}^{-1}$  mode increases in intensity. The intensity of the 930  $\text{cm}^{-1}$  mode increases and the feature broadens substantially, although this is likely due to the formation of a small amount of second-layer propylene. At higher exposures, the multiplicity of peaks noted on clean Pd(111) appears, but now at lower propylene exposures than on the clean surface. These additional features are almost completely removed on heating to 190 K (Fig. 4(e)) where the 1015 and 980- $\text{cm}^{-1}$  features are still evident. Heating to 230 K removes all of the remaining second-layer propylene. Further warming to 325 K produces peaks at 2931, 1753 and 937  $\text{cm}^{-1}$ , essentially identical to those formed by heating propylene on clean Pd(111) to 325 K (Fig. 2(i)).

### 3.3. Adsorption of propylene on Pd(111) at high temperatures

Propylidyne species have been found on the (111) surfaces of group VIII metals [5]. The Pd(111) surface was exposed to varying amounts of propylene at 100 K and above 300 K and the resulting 2 amu desorption spectra are displayed in Fig. 5. For comparison, the 2 amu spectrum due to ethylidyne decomposition (top spectrum), with a

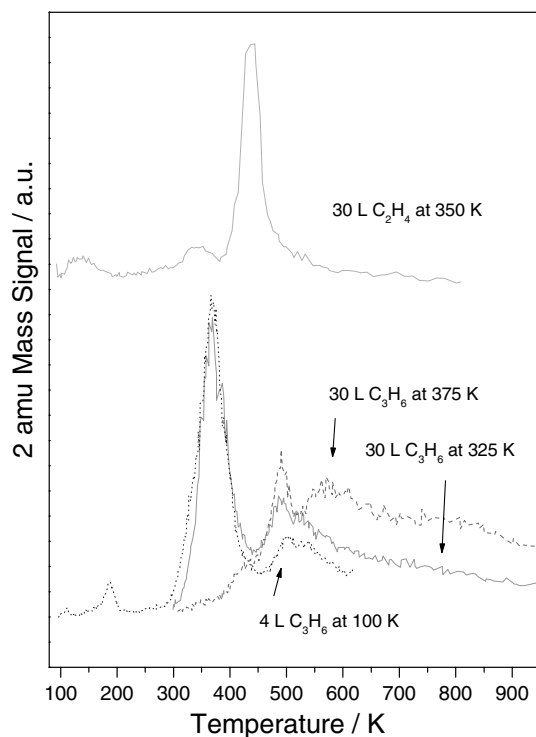


Fig. 5. TPD spectra comparing the decomposition of propylidyne and  $\eta^1$ -allyl species after adsorption at 100, 325, and 375 K. The TPD spectra of hydrogen from an ethylidyne saturated surface is shown for comparison.

coverage of 0.25 ML, is shown. The 2 amu spectrum following propylene adsorption at 100 K (dotted line) reproduces the spectrum shown in the inset of Fig. 1, and spectra are also displayed following a 30 L propylene exposure at 325 K (solid line) and 375 K (dashed line). It is clear that a considerable amount of hydrogen, the product of propylene dehydrogenation, evolves from the surface at  $\sim 360 \text{ K}$ , a temperature slightly higher than that for desorption of hydrogen from a clean surface. If the sample is exposed to propylene at 325 K, it is observed that the 360 K hydrogen peak intensity remains constant, while the 500 K feature continues to grow. It is then inferred that the peak at  $\sim 360 \text{ K}$  and desorption above 450 K correspond to decomposition of at least two different, strongly bound species. When the dosing temperature is elevated to 375 K, the 500 K peak intensity increases further, and a new series of hydrogen

peaks are observed at temperatures above 550 K. The RAIRS spectrum corresponding to an exposure of 30 L at 325 K is shown in Fig. 6(a) using the clean surface as a background. The most intense feature observed is in the C–H stretching region at  $2924\text{ cm}^{-1}$ , with weaker peaks at 2960, 2860, 1710,  $\sim 1450$ ,  $\sim 1400$  and  $1105\text{ cm}^{-1}$ .

It has been shown previously that ethylene could adsorb onto the Pd(111) surface in spite of the presence of an ethylidyne overlayer [3]. A Pd(111) surface was therefore exposed to 30 L of propylene at 300 K and then further exposed to propylene at 80 K. The resulting infrared spectra are displayed in Fig. 6(b)–(d), in this case, using the propylidyne-covered surface as a background. Very weak features are evident at  $\sim 934$ , 1450 and

$2892\text{ cm}^{-1}$  for low propylene exposures (0.5 L, Fig. 5(b)). The features found at higher exposures on clean (Fig. 2(e)), and hydrogen-covered (Fig. 5(c) and (d)) Pd(111) are clearly observed for exposures larger than 1.3 L (Fig. 6(d)–(e)) with the onset of these features apparent at an exposure of 1 L, along with a negative excursion at  $\sim 2924\text{ cm}^{-1}$ . The negative feature implies that the propylidyne has been perturbed, but not removed, by the presence of additional propylene since this feature disappears on heating the sample to  $\sim 220\text{ K}$  (Fig. 6(f)). The corresponding TPD spectrum is displayed in Fig. 7 and compared with those for propylene on clean and hydrogen-covered Pd(111). Propylene desorption from propylidyne-covered Pd(111) displays a feature at  $\sim 190\text{ K}$  seen on clean and hydrogen-covered Pd(111), but in the case of the propylidyne-covered surface, is much broader, and shifted slightly in temperature. An additional propylene desorption state is

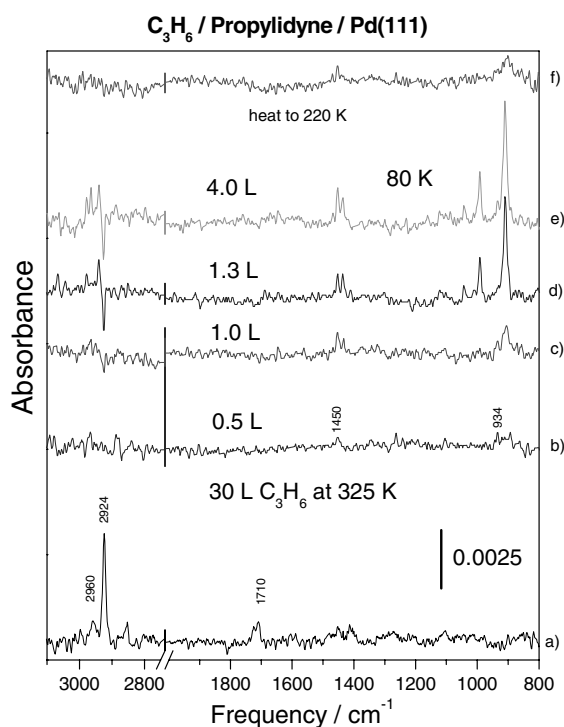


Fig. 6. Reflection-absorption infrared spectra of (a) propylidyne on Pd(111) formed by exposing Pd(111) to 30 L of propylene at 325 K and exposing propylidyne-covered Pd(111) to propylene at 80 K; (b) 0.5 L, (c) 1.0 L, (d) 1.3 L and (e) 4.0 L. Spectrum (f) shows the result of heating to 220 K. Spectra (b)–(f) were collected using spectrum (a) (of propylidyne-covered Pd(111)) as a background.

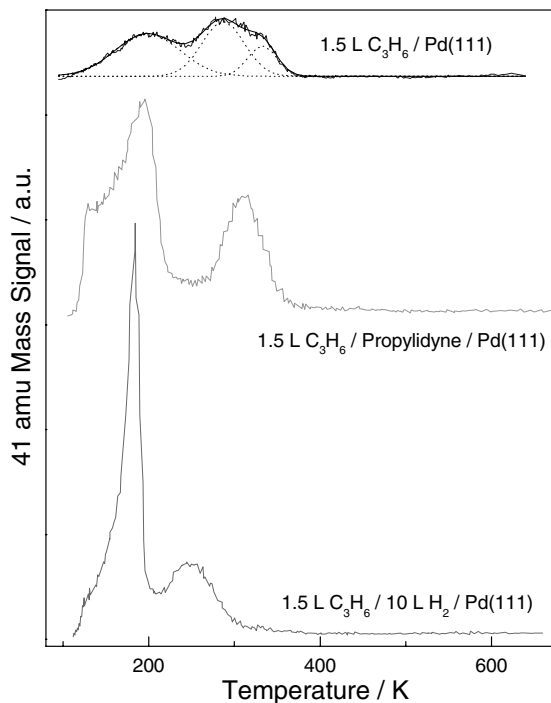


Fig. 7. TPD spectra comparing the behavior of propylene (1.5 L) on clean Pd(111) with that on hydrogen-covered Pd(111) (hydrogen exposure, 10 L) and on propylidyne-covered Pd(111).

detected at  $\sim 310$  K. This peak is present even when a propylidyne surface is formed at 325 K and not exposed to propylene at lower temperature.

#### 4. Discussion

##### 4.1. Adsorption of propylene on Pd(111) at low temperatures

Previous kinetic studies of the adsorption of propylene on Pd(111) by LITD showed the appearance of only two propylene desorption states at  $\sim 180$  and 300 K, and these were assigned to multilayer and monolayer desorption respectively [11]. Fig. 1 shows that propylene desorbs from the Pd(111) surface in several states at  $\sim 200$ , 280 and 340 K with a sharp desorption state appearing at 190 K and lower temperatures at higher exposures.

The species formed at low propylene exposures on clean Pd(111) at 80 K is characterized by vibrational features at 930, 1014, 1439 and 2890  $\text{cm}^{-1}$  (Fig. 2(b)). It is clear that these frequencies do not correspond to those in gas-phase propylene indicating some degree of di- $\sigma$  rehybridization of propylene on the Pd(111) surface. Curiously, in TPD the broad, low-temperature ( $\sim 200$  K) desorption state appears to populate prior to the higher-temperature states. A similar low-temperature state at  $\sim 200$  K has been detected on Pt(111) [6]. These two states cannot be due to propylene adsorbed at different sites on the surface since, in this case, the most stable site would be

occupied first. In the case of propylene adsorption on Pt(111), a “V-shaped” adsorption state was identified at low coverages, while at high coverages the appearance of a state with the methyl group aligned perpendicular to the surface was observed [5]. The appearance of an infrared peak at 1116  $\text{cm}^{-1}$  is detected at high propylene coverages on Pd(111) (Fig. 2(d)), which remains up to 230 K. This feature could be similarly associated with the  $\nu(\text{C}-\text{CH}_3)$  mode of a more perpendicular di- $\sigma$  species.

In order to assign infrared features, RAIRS spectra of adsorbed olefins can be compared with the infrared spectra of olefin-containing organometallics. The spectral features for propylene on clean Pd(111) are compared with those obtained for  $\text{Os}_2(\text{CO})_8-(\mu_2-\mu^1, \mu^1-\text{C}_3\text{H}_6)$  [19] and propylene on Pt(111) and Ni(111) surfaces in Table 1. The majority of the features agree reasonably well with those of the osmium cluster. Features at 2920 and 2820  $\text{cm}^{-1}$  detected using second-harmonic generation (SHG) have been assigned to di- $\sigma$ -bonded species on Pt(111) [8]. While the higher of these two frequencies is close to that observed on Ni(111) (2906  $\text{cm}^{-1}$ ), Pt(111) (2916  $\text{cm}^{-1}$ ), and Pd(111) (2931  $\text{cm}^{-1}$ ), it is not particularly diagnostic, being common to several species [20]. However, these observations are consistent with the presence of a less rehybridized propylenic species on clean Pd(111) than on nickel or platinum. The increase in C–C stretching frequency on Pd(111) compared to the other metals immediately indicates a higher C–C bond order, resulting

Table 1

Comparison of the RAIRS spectrum of propylene adsorbed on Pd(111) at 80 K (Fig. 4(a)) with propylene on Pt(111), Ni(111) and the vibrational spectrum of  $\text{Os}_2(\text{CO})_8-(\mu_2-\mu^1, \mu^1-\text{C}_3\text{H}_6)$

Mode	Frequency ( $\text{cm}^{-1}$ )			
	$\text{Os}_2$ cluster <sup>a</sup>	$\text{C}_3\text{H}_6/\text{Pt}(111)^b$	$\text{C}_3\text{H}_6/\text{Ni}(111)^b$	$\text{C}_3\text{H}_6/\text{Pd}(111)^c$
$\nu_{\text{CC}}$	901/893	862	871	930
$\rho(\text{CH}_3)$	1022	1015	1029	1014
$\tau(\text{CH}_2)$	1057	1038	–	–
$\nu(\text{C}-\text{CH}_3)$	1110	1088	1142	1116
$\delta(\text{CH}_2)$	1439	1438	1445	1439
$\nu(\text{CH})$	2902	2883	2860	2890
$\nu_3(\text{CH}_3)2\delta_{\text{as}}(\text{CH}_3)$	2932	2916	2906	–

<sup>a</sup> Taken from Ref. [19].

<sup>b</sup> Taken from Refs. [5,19].

<sup>c</sup> This work.



in a more planar species. This suggests that the order of the hybridization on the three surfaces is  $\text{Pt}(111) > \text{Ni}(111) > \text{Pd}(111)$ .

The  $1014\text{-cm}^{-1}$  feature formed after a propylene exposure higher than 1.4 L is still present after heating to 230 K, but disappears on heating to 270 K (Fig. 2(g) and (h)) to be replaced by the broad feature at  $937\text{ cm}^{-1}$ . This first implies that the surface species exhibiting the  $1014\text{-cm}^{-1}$  mode can desorb in the state centered at  $\sim 200$  K, but also converts on heating to 270 K to another species characterized by the broad  $937\text{ cm}^{-1}$  peak. The latter peak is likely to be due to two species since heating to 325 K, when the high-temperature desorption state is complete, leaves behind a sharper peak at  $922\text{ cm}^{-1}$  and a weak feature at  $\sim 1745\text{ cm}^{-1}$ . This species presumably ultimately thermally decomposes to desorb hydrogen at  $\sim 360$  K (Fig. 3). The nature of the species formed on the clean surface exhibiting the broad infrared feature at  $\sim 937$  and  $1745\text{ cm}^{-1}$  (Fig. 2(i)), and desorbing at  $\sim 340$  K (Fig. 7), is difficult to establish. However, a study of allylic groups on  $\text{Pt}(111)$  showed that these are easily formed and even more stable than di- $\sigma$  propylene [21]. The vibrational feature at  $1745\text{ cm}^{-1}$  would then correspond to the C=C stretching mode of an  $\eta^1$ -allyl species. The formation of allylic species on  $\text{Pd}(111)$  would also explain the appearance of two high-temperature peaks in the TPD data in Fig. 1 (and reproduced in Fig. 7), corresponding to desorption of di- $\sigma$  propylene (280 K) and propylene from allylic species reacting with hydrogen remaining on the surface (335 K).

The overall picture that emerges is that di- $\sigma$  adsorbed propylene initially forms on  $\text{Pd}(111)$  at 80 K. On heating, a portion of this propylene desorbs in the broad feature at  $\sim 200$  K (Fig. 1), and simultaneously converts into a more stable di- $\sigma$ -bonded species with a more perpendicular C-CH<sub>3</sub> group, yielding an additional vibrational mode at  $1116\text{ cm}^{-1}$ , which desorbs at  $\sim 280$  K. Further heating forms a proposed allylic species. A small portion of this species rehydrogenates at  $\sim 340$  K, while the majority dehydrogenates at  $\sim 360$  K. A small amount of hydrogen is detected above this temperature, and the origin of this will be discussed in greater detail below.

#### 4.2. Second-layer propylene adsorption

As the propylene exposure at 80 K increases further, additional features appear on clean (Fig. 2(e)), hydrogen-covered (Fig. 4(d)), and propylidyne-covered (Fig. 5(e))  $\text{Pd}(111)$ . In all cases, this species desorbs in a sharp feature at  $\sim 190$  K, although the desorption temperature is slightly higher on the propylidyne-covered surface. The RAIRS frequencies associated with this state are identical on all of the surfaces and can be straightforwardly assigned to weakly adsorbed propylene by comparison with the frequencies for gas-phase [22] and solid propylene [23], and the assignments are displayed in Table 2. Weakly adsorbed propylene desorbs at  $\sim 190$  K from  $\text{Pd}(111)$  and a similar species thermally desorbs at 180 K from  $\text{Pt}(111)$  [6]. This has been assigned to the desorption of propylene adsorbed in a second layer and a similar assignment is made here. The conjecture is confirmed by the data of Fig. 6, which show the effect of adsorbing propylene onto a propylidyne-covered surface. Intense features appear due to  $\pi$ -bonded propylene adsorbed on top of the carbonaceous layer. Similar second-layer desorption has been observed for ethylene on  $\text{Pd}(111)$  [4] and  $\text{Pt}(111)$  [24]. It has also been shown that such second-layer adsorption

Table 2  
Vibrational assignment for the RAIRS of high coverages of propylene on  $\text{Pd}(111)$  (Fig. 2(e) and (f)), hydrogen-covered  $\text{Pd}(111)$  (Fig. 4(c) and (d)) and propylidyne-covered  $\text{Pd}(111)$  (Fig. 6(d) and (e)) at 80 K

Frequency ( $\text{cm}^{-1}$ )		
$\text{C}_3\text{H}_6/\text{Pd}(111)$	Solid/gas-phase propylene <sup>a,b</sup>	Assignment <sup>c</sup>
3081	-/3081	$\nu_a(\text{CH}_2)$
3067	3064/3067	Overtone
2980	2970/2979	$\nu_s(\text{CH}_2)$
2965	-/2960	$\nu_a(\text{CH}_3)$
2942	2934/2942	Overtone
1647	1647/1647	$\nu(\text{C}=\text{C})$
1452	1453/1448	$\delta_a(\text{CH}_3)$
1437	1437/1416	$\text{CH}_2$ deformation
991	995/996	$\text{CH}_3$ rock
937	933/936	CH bend
910	911/919	$\nu(\text{C}-\text{CH}_3)$

<sup>a</sup> Solid-phase frequencies taken from Ref. [23].

<sup>b</sup> Gas-phase frequencies taken from Ref. [22].

<sup>c</sup> Assignments based on Ref. [20].

occurs on CO-saturated Pd(111) [25]. As noted above, the vapor pressures of both ethylene and propylene at 80 K are above the background pressure of  $1 \times 10^{-10}$  Torr at which these experiments were performed. This indicates that the interaction between the second and first layer is larger than the Van der Waals' interactions in the gas-phase. The desorption activation energy of propylene in the second layer can be estimated using the Redhead equation [26] assuming a desorption pre-exponential factor of  $1 \times 10^{13}$  s $^{-1}$  and a heating rate of 7 K/s to yield a desorption activation energy of  $\sim 46$  kJ/mol. The heat of sublimation of propylene is  $\sim 34$  kJ/mol. Thus, the presence of the higher-temperature, second-layer feature implies that this bonds more strongly to the chemisorbed overlayer than to gas-phase propylene implying larger Van der Waals' interaction with the chemisorbed overlayer. One possible origin for a larger interaction could be the increase in dipole moment of the first layer due to its interaction with the surface. Gas-phase propylene has a dipole moment of 0.366 D. This will be modified by adsorption to the surface. For example, a saturated overlayer of ethylidyne on Pd(111) gives a work-function change of 0.7 eV [27] and, using the saturation coverage of ethylidyne ( $\theta_{\text{sat}} = 0.25$  [25]), gives a dipole moment of  $\sim 0.33$  D. Similar dipole moment enhancements for propylene or propylidyne on the surface will clearly lead to stronger dipole-dipole interactions between the overlayer and second layer than between gas-phase propylene molecules enhancing the bonding of the second-layer molecules to the surface. Since dipole-dipole interactions vary as  $\sim 1/r^3$  where  $r$  is the distance between the molecules, the interaction between the third and first layer will only be slightly enhanced relative to the interaction between the second layer and the chemisorbed overlayer. Such a residual enhancement may account for the 110 K desorption feature seen at higher propylene exposures (Fig. 1).

#### 4.3. Propylene adsorption on hydrogen-covered Pd(111)

It has been shown previously that the pre-adsorption of hydrogen on Pd(111) causes ethylene to adsorb in a  $\pi$ -bonded configuration, and com-

pletely eliminates the di- $\sigma$  species present on a clean Pd(111) surface [4]. In the case of propylene, two new features are detected in the RAIRS spectrum at 2931 and 980 cm $^{-1}$  (Fig. 4), but all the features present on the clean surface remain, although with a smaller intensity. The adsorption of undistorted propylene on a flat (111) surface via the propylenic  $\pi$  orbitals would result in significant steric repulsion between the surface and the methyl group. Recent quantum calculations for propylene on Pt(111) have confirmed this and show unstable  $\pi$ -bonded configurations with the methyl group oriented away from the surface [28]. While the vibrational frequencies are similar for clean (Fig. 2) and hydrogen-covered (Fig. 4) Pd(111), there are clear differences in the relative intensities of the modes. In particular, the 1014 cm $^{-1}$  (methyl rocking) mode is much more intense on the clean than the hydrogen-covered surface, indicating that the methyl mode is either much more parallel to the surface on clean Pd(111), or that there are more than one species. The 980 cm $^{-1}$  infrared feature has been assigned to the methylene twisting mode of a weakly adsorbed species on Pt(111) [5].

The changes in orientation or hybridization observed above also affect the heat of adsorption on the surface resulting in a shift in desorption temperature from  $\sim 280$  K on clean Pd(111) to  $\sim 230$  K on the hydrogen-covered surface (Fig. 3). Both desorption temperatures are substantially lower than for di- $\sigma$ -bonded ethylene on Pd(111), which desorbs at  $\sim 320$  K at low coverages [27]. However, the lower propylene desorption temperature is within the range found for the desorption of first layer propylene on Pt(111) ( $\sim 230$ – $240$  K) [6]. The pre-adsorption of hydrogen completely suppresses the high-temperature desorption of propylene due to the reaction of allylic species above 300 K.

Propane desorption is found following propylene adsorption on hydrogen-covered Pd(111) (Fig. 3). Since neither the reaction order nor the pre-exponential factor are known for this state, the desorption activation energy was estimated by plotting  $\ln(\text{rate})$  versus  $1/T$  for the leading-edge region of the desorption spectrum, where the reactant coverages remain, to a good approximation, constant. The rate was measured from the

height of the desorption profile above baseline. The value obtained in this way was  $3.4 \pm 0.4$  kcal/mol, which is, within experimental error, essentially the same as for the hydrogenation of ethylene to ethane on Pd(1 1 1) ( $3.0 \pm 0.3$  kcal/mol, [17]). The values for the activation energy of these reactions on supported Pd have been reported to be  $\sim 8$  and  $\sim 11$  kcal/mol for the hydrogenation of ethylene and propylene respectively [29].

#### 4.4. Dehydrogenation of propylene on Pd(1 1 1)

It has been shown previously [5,6] that the room-temperature chemistry of propylene on close-packed group VIII metals is similar to that of ethylene since alkylidyne species are formed in both cases. This is studied by the RAIRS spectrum shown in Fig. 6(a) following the adsorption of 30 L of propylene on Pd(1 1 1) at 325 K, and the assignments of the observed features compared to those found on Pt(1 1 1) [6] are shown in Table 3. The agreement in peak positions for propylidyne on the two surfaces is good. The only peak that has no counterpart in the spectrum for propylidyne on Pt(1 1 1) is that at  $\sim 1710$   $\text{cm}^{-1}$ , which has been associated above with the presence of  $\eta^1$ -allylic species. The shift from 1745 to 1710  $\text{cm}^{-1}$  presumably arises due to interaction with the surrounding propylidyne species. There are also substantial differences in the relative intensities between the two propylidyne spectra on Pd(1 1 1) and Pt(1 1 1), particularly in the C–H stretching region. The  $\nu_a(\text{CH}_3)$  mode is the most intense for

propylidyne on Pt(1 1 1), while the  $\nu_s(\text{CH}_3)$  mode is the most intense on Pd(1 1 1). This connotes a substantial difference in the orientation of the C–CH<sub>3</sub> bond for these species, which is oriented closer to perpendicular to the surface for propylidyne on Pd(1 1 1) than Pt(1 1 1), probably due to the crowding of the surface by the co-adsorbed  $\eta^1$ -allyl species. It should also be noted that there is no evidence for the formation of propylidyne species when propylene, adsorbed at low temperatures, is heated to room temperature (Fig. 2), while propylidyne formation was found when propylene/Pt(1 1 1) was heated. The formation of allylic species on Pd(1 1 1) was found either by warming propylene adsorbed at low temperature or by dosing propylene at high temperature. The main reaction pathways for propylene on clean and hydrogen-covered Pd(1 1 1) are summarized schematically in Scheme 1.

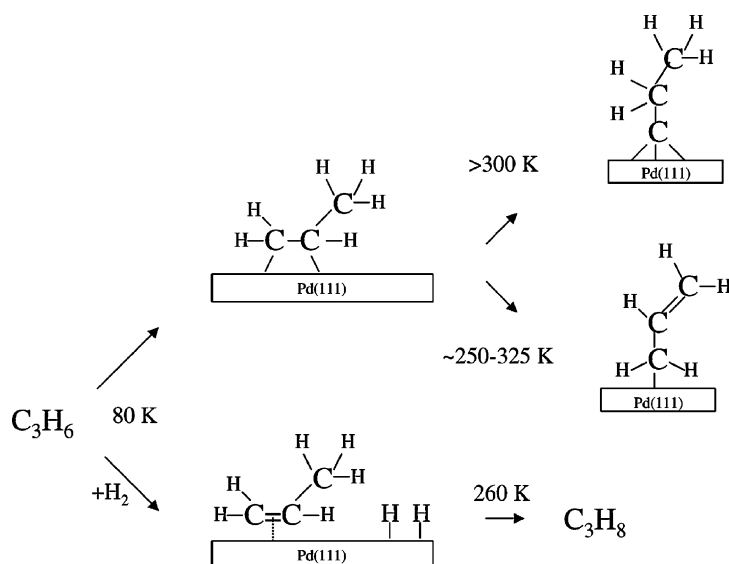
It has been found previously that ethylene can adsorb onto the palladium surface on ethylidyne-covered Pd(1 1 1) [3]. The possibility of propylene adsorption on top of a propylidyne-covered Pd(1 1 1) surface was also explored. The resulting TPD spectra are displayed in Fig. 7 and compared to those on clean and hydrogen-covered Pd(1 1 1), where the spectrum of propylene on propylidyne-covered Pd(1 1 1) exhibits two states at  $\sim 310$  K and a broad state at  $\sim 190$  K. The latter state corresponds to desorption of second-layer propylene discussed above. The state at  $\sim 310$  K has been related above to the presence of allylic species. Neither a 280 K desorption state is observed in TPD from a propylidyne-covered surface nor a 1014  $\text{cm}^{-1}$  mode observed in RAIRS, both indicative of di- $\sigma$  propylene adsorption on the surface. The possibility of weakly adsorbed ( $\pi$ -bonded) propylene on the surface is also ruled out by the lack of both a low temperature TPD desorption peak and an infrared feature at 980- $\text{cm}^{-1}$ .

The RAIRS spectra of propylene on propylidyne-covered Pd(1 1 1) are displayed in Figs. 6(b)–(e). Note that there is no feature at  $\sim 1014$   $\text{cm}^{-1}$  found both on clean (Fig. 1) and hydrogen-covered Pd(1 1 1) (Fig. 4) assigned to di- $\sigma$ -bonded propylene. This indicates that the presence of a propylidyne plus allylic overlayer precludes the adsorption of propylene onto the surface. In

Table 3

Assignments for the RAIRS spectrum of propylene adsorbed on Pd(1 1 1) at 300 K (Fig. 6(a)), compared to the spectrum of propylidyne on Pt(1 1 1) [5]

Assignment	Propylene/Pd(1 1 1) 30 L, 325 K	Propylene/Pt(1 1 1) 5.0 L, 275–350 K
$\nu_a(\text{CH}_3)$	2960 m	2960 vs
$\nu_s(\text{CH}_3)$	2924 s	2917 s
$2\delta_a(\text{CH}_3)$	2860 m	2860 m
$\gamma_a(\text{CH}_3)$	1450	1450
$\delta(\text{CH}_2)$	1410	1408
$\delta_s(\text{CH}_3)$	–	1374
$\nu(\text{C–C})$	1105	1104
$\rho(\text{CH}_3)$	–	1079
$\rho(\text{CH}_3)$	–	1041



Scheme 1. Major reactions of propylene on Pd(1 1 1).

contrast, it was found that the analogous adsorption of ethylene on ethylidyne-covered Pd(1 1 1) not only was allowed, but also showed no effect on the state of ethylene hybridization, which was di- $\sigma$ -bonded on both clean [4] and ethylidyne-covered Pd(1 1 1) [3] and was only affected by the presence of co-adsorbed hydrogen.

As propylidyne-covered Pd(1 1 1) is exposed to further propylene, a set of features corresponding to second-layer propylene becomes evident (compare with Table 2). Accompanying these features, a negative excursion is noted at  $2924\text{ cm}^{-1}$ , corresponding to the most intense feature of propylidyne. This indicates that the propylidyne is being affected by the presence of the additional propylene on top of it and provides additional evidence for its adsorption in the second layer. This feature appears not to shift, but merely decrease in intensity. Its relatively large intensity was ascribed to the C–CH<sub>3</sub> bond being oriented close to perpendicular to the surface, so that the intensity decrease suggests that the methyl group reorients so that it moves closer to the surface in the presence of second-layer propylene. This effect is completely reversible as indicated by the lack of negative excursions when the surface is heated to remove second-layer propylene. The formation of

propylidyne at temperatures above 360 K, where hydrogen TPD indicates that the decomposition of allylic species is complete, results in the appearance of hydrogen desorption peaks above 550 K, indicating the stepwise dehydrogenation of propylidyne, as was found on Pt(1 1 1) [30].

## 5. Conclusions

Propylene adsorbs in a di- $\sigma$  configuration on clean Pd(1 1 1). When the surface is heated, molecular desorption and dehydrogenation take place. The main product of dehydrogenation is an  $\eta^1$ -allyl species, which remains on the surface even after the molecular propylene has desorbed. At high temperatures, propylidyne species are formed, which decomposes at temperatures above 550 K. The pre-adsorption of hydrogen results in the weakening of the propylene bonding to Pd(1 1 1). The conversion of di- $\sigma$  to  $\pi$ -bonded adsorption induced by the presence of hydrogen is not complete, in contrast to the case of ethylene, due to steric hindrance caused by the methyl group. Hydrogenation of propylene to propane proceeds in TPD experiments with an activation energy of  $3.4 \pm 0.4\text{ kcal/mol}$ . A combination of  $\eta^1$ -allyl and

propylidyne species are formed following propylene adsorption at 300 K, resulting in a very crowded surface that precludes the subsequent adsorption of any molecular propylene.

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