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Surface Science 391 (1997) 145–149

surface science

## Reflection–absorption infrared spectroscopy of ethylene on palladium(111) at high pressure

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Received 17 February 1997; accepted for publication 2 June 1997

### Abstract

The adsorption of ethylene adsorbed on Pd(111) at  $\sim 300$  K is studied using reflection–absorption infrared spectroscopy which confirms the formation of an ethylidyne species because of the presence of vibrational mode at  $1329\text{ cm}^{-1}$  with a less-intense peak at  $1089\text{ cm}^{-1}$ . The  $1329\text{ cm}^{-1}$  methyl mode is well away from any vibrational modes of gas-phase ethylene, which allows the spectrum of the surface species to be collected in the presence of high pressures (up to  $\sim 1$  torr) of ethylene. These results reveal that ethylidyne is present on the surface in the presence of gas-phase ethylene and that there may be a slight increase in coverage. The width of the line, however, increases substantially by  $5.3 \pm 0.4\text{ cm}^{-1}\text{ torr}^{-1}$ . This effect is ascribed to a loss of order in the ethylidyne layer probably caused by co-adsorption of ethylene. © 1997 Elsevier Science B.V.

*Keywords:* Alkenes; Chemisorption; Infrared absorption spectroscopy; Low index single crystal surfaces; Palladium; Reflection spectroscopy; Single crystal surfaces

It has been suggested previously that transition-metal catalyzed hydrocarbon reactions proceed in the presence of a hydrocarbon layer. The initial suggestion was based on a post-mortem analysis of a platinum single crystal model catalyst following ethylene hydrogenation where an ordered ethylidyne layer was found [1]. Thus, information on the nature of a catalytic surface *during* reaction under an external pressure of several torr is crucial in determining how the catalytic reaction proceeds. This nature of the catalytically active surface has been probed in the presence of a high external pressure ( $\sim 1$  torr) in a number of

ways; for example, using sum–frequency generation (SFG) [2] which is inherently surface sensitive, fluorescence yield near-edge spectroscopy (FYNES) [3] and infrared (IR) spectroscopy [4]. SFG has revealed the presence of ethylidyne species on the surface during ethylene hydrogenation. Unfortunately, this technique requires extremely sophisticated equipment and is difficult and time consuming. Over the last few years, reflection–absorption IR spectroscopy has developed into a technique which, while not entirely routine, has evolved to the point that it is relatively accessible to most surface analysis laboratories. It also has the advantage that the physical principles and data analysis are extremely well developed. Unfortunately, it is not inherently surface sensitive so that interference from the gas phase can become a problem at higher gas pressures.

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There are several ways in which the above problems can be overcome. In cases where the adsorbate desorbs to leave a clean surface, merely heating the sample in the high-pressure ambient forms a clean surface to provide a background spectrum in the presence of a high pressure of gas [4]. This is then used to collect a background spectrum. The sample is then allowed to cool to the experimental temperature, the spectrum of an adsorbate-covered surface is collected, and rationing the two allows the adsorbate spectrum to be collected. This strategy has been used to advantage to follow the chemistry of CO and NO on Pd(111) [4]. Alumina-supported, model palladium catalysts with relatively high surface areas have been used [5]; these increase the surface sensitivity by a factor of  $\sim 20$  relative to a planar single crystal sample, which allows IR spectra of surface species to be easily collected in the presence of up to  $\sim 1$  torr of ethylene. Unfortunately, the homogeneity of the model single crystal catalyst is lost in this case.

Ethylidyne, and both  $\pi$  and di- $\sigma$ -bonded ethylene, have been detected on Pt(111) in the presence of pressures of up to  $\sim 5 \times 10^{-5}$  torr of ethylene [6]. Unfortunately, this pressure is several orders of magnitude below that which could be considered a catalytic regime. We have, however, extended this approach by studying a system where the surface species are sufficiently different from the gas-phase precursor that their peaks can be identified in the windows between the gas-phase features and which therefore allows their spectra to be collected in the presence of an external gas-pressure. We have used this strategy to examine the nature of the species present on the surface of a palladium single crystal in the presence of a high pressure (up to  $\sim 1$  torr) of ethylene – much higher pressures than have been attained previously on a model single crystal catalyst. Unfortunately, the reactivity of the surface species with high pressures of hydrogen could not be probed using the Pd(111) single crystal used for these experiments because of the tendency of palladium to absorb hydrogen. We are currently exploring the possibility of carrying out these reactions using foils.

The IR sample cell used for these experiments is constructed from a  $2\frac{3}{4}$ " flange, six-way cross,

which had been modified by moving one flange by  $\sim 20^\circ$  to allow IR radiation to impinge on the sample with the optimal  $80^\circ$  IR incidence angle. The cell is attached to the main chamber via a gate valve, which, when closed, completely isolates the IR cell from the ultrahigh vacuum (UHV) chamber and, when open, allows sample transfer into it.

The IR optical train is mounted onto a 3"-thick optical table that is mounted to the same frame as the UHV chamber. Light from a Midac M2000, Fourier-transform IR spectrometer is steered to an off-axis parabola mirror placed  $\sim 10$  cm from the sample. Test experiments using visible radiation shows an image size of approximately 0.5 cm. Plane-polarized radiation is obtained by passing the light through a Harrick polarizer made by placing chevrons of germanium at the Brewster angle. The whole of this optical path is enclosed in plexiglass boxes which are purged with dry air from a Whatman air drier or using nitrogen boil off from a MVE Cryogenics Dewar. Light that is reflected from the sample is steered via two concave mirrors to a liquid-nitrogen-cooled, mercury cadmium telluride (MCT) IR detector (Graseby Infrared, USA).

The IR spectrometer is controlled using SpectraCalc software running on a microcomputer. This collected and transformed the signal and has capabilities for smoothing and plotting the data. The background and adsorbate-covered spectra were collected for  $\sim 1000$  scans depending of the desired level of signal:noise ratio with a spectral resolution of  $4 \text{ cm}^{-1}$ . The IR radiation is furnished by an air-cooled Globar source incorporated into the Midac spectrometer.

The palladium single crystal sample was cleaned using standard procedure which consisted primarily of heating in oxygen ( $1 \times 10^{-6}$  torr, 1000 K) to remove carbon and annealing to 1150 K to desorb any remaining oxygen [7]. This resulted in further segregation of carbon to the surface of the sample, which could then be removed by repeating the above procedure. Since the carbon KLL Auger feature is obscured by an intense palladium peak, a more effective method for gaging sample cleanliness is to dose the sample with oxygen and perform

a temperature-programmed desorption experiment monitoring both CO (28 amu) and oxygen (32 amu). A dirty surface was indicated by the desorption of CO. This signal diminished as the cleaning procedure progressed so that ultimately a clean surface was indicated by the desorption of only oxygen. The ethylene (Matheson, 99.9%) was transferred from the cylinder into a glass bottle and further purified by repeated bulb-to-bulb distillations and the cleanliness monitored using IR spectroscopy and from its mass spectral fragmentation pattern. Neither of these revealed any impurities after this purification procedure.

Fig. 1a displays the RAIRS spectrum collected following ethylene adsorption (80 L) on Pd(111) at 300 K. The ethylene was dosed via a dosing source located in the IR cell, which allowed the sample to be dosed rapidly without compromising the background pressure. The spectrum exhibits an intense feature at  $1329\text{ cm}^{-1}$  with a less-intense peak at  $1089\text{ cm}^{-1}$ , is essentially identical to that found using HREELS [8] and is very close in

frequency to the spectra formed by adsorption of ethylene on Pt(111) [9] or Rh(111) [10], which have been assigned to the formation of an adsorbed ethylidyne species. The  $1329\text{ cm}^{-1}$  mode is due to a methyl bending vibration and the  $1089\text{ cm}^{-1}$  feature to a carbon-carbon stretching mode. The frequency of the  $1329\text{ cm}^{-1}$  mode is almost exactly the same for ethylidyne on rhodium and palladium, whereas the  $1089\text{ cm}^{-1}$  mode is at a slightly higher frequency ( $1115\text{ cm}^{-1}$ ) on platinum. This suggests a slightly weaker carbon-carbon bond on palladium than on platinum. Fig. 1b shows the spectrum obtained in the presence of an external pressure (0.3 torr) of ethylene showing the gas-phase features. This indicates that there is a window that allows the  $1329\text{ cm}^{-1}$  methyl bending mode to be detected in the presence of an external gas pressure.

The spectrum of the most intense  $1329\text{ cm}^{-1}$  peak taken as a function of ethylene pressure up to a pressure of 1 torr is displayed in Fig. 2. The peak position is exactly identical in all of these

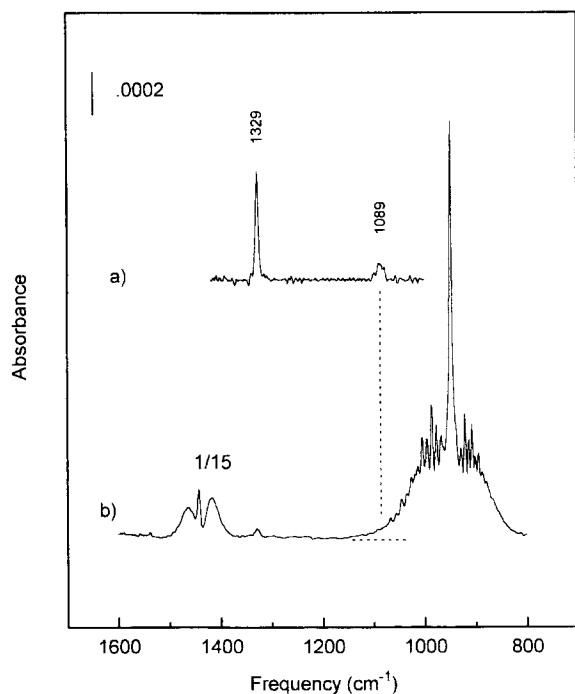


Fig. 1. (a) RAIRS spectrum collected following 80 L exposure of ethylene to Pd(111) at 300 K; (b) a RAIRS spectrum of the surface of Pd(111) in the presence of 0.3 torr of ethylene.

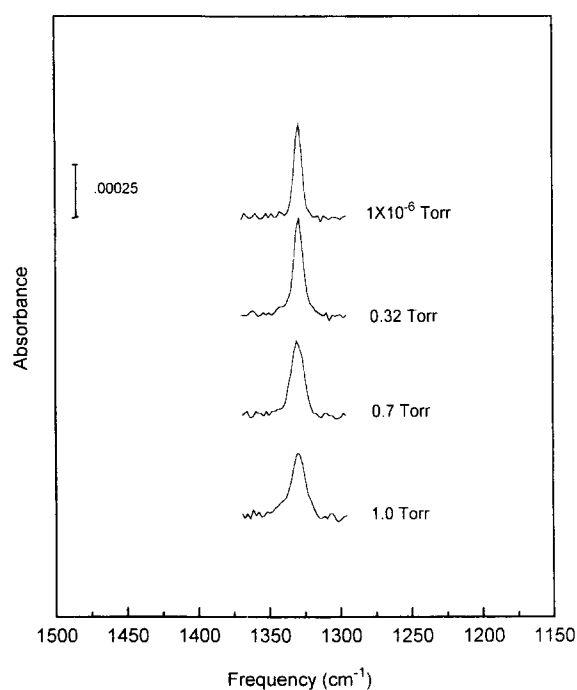


Fig. 2. A series of RAIRS spectra of a Pd(111) surface in the presence of ethylene at various pressures. The corresponding pressures are marked adjacent to each spectrum.

data up to 1.0 torr indicating the continued presence of ethylidyne under these conditions. The  $1089\text{ cm}^{-1}$  feature is not shown in these data since it becomes obscured by gas-phase features as the pressure increases. It is clear, however, that the shape of the spectrum changes as the pressure increases so that the peak intensity decreases as the pressure increases and correspondingly the width at half maximum increases. These changes are documented in Figs. 3 and 4, which plot the integrated peak area of the  $1329\text{ cm}^{-1}$  peak (Fig. 3) and its variation in full-width at half maximum (Fig. 4), respectively, as a function of ethylene pressure. There is a slight increase in integrated peak area as the ethylene pressure increases by approximately 7% as the pressure changes to 1.0 torr. Note, however, that the error in the area measurement is sufficiently large that it is not clear whether this is statistically significant although there does seem to be a tendency to accommodate slightly more ethylidyne on the sur-

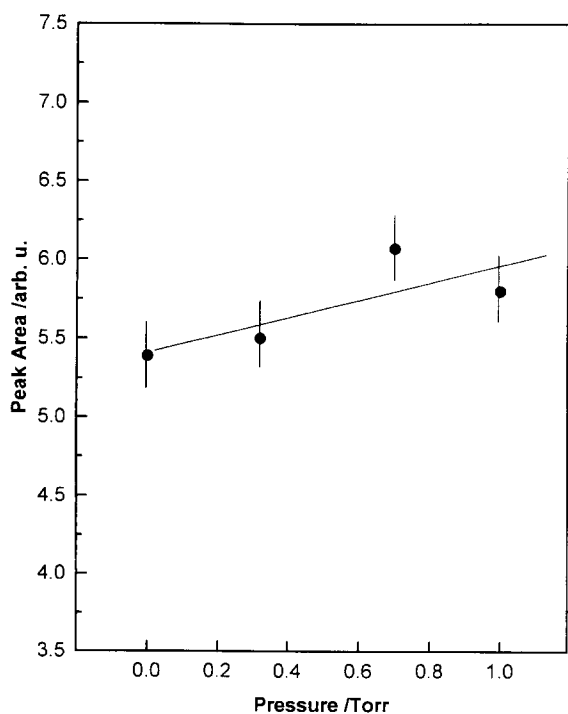


Fig. 3. A plot of the integrated intensity of the  $1329\text{ cm}^{-1}$  feature in the RAIRS spectrum of Pd(111) in the presence of ethylene plotted as a function of ethylene pressure.

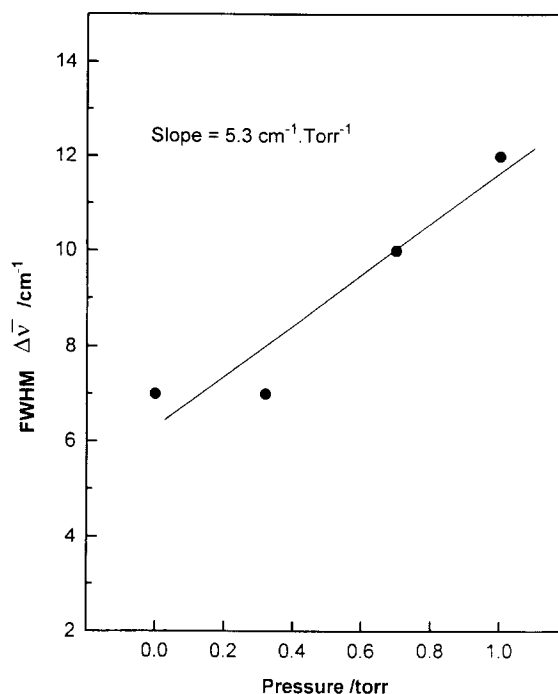


Fig. 4. A plot of the full width at half maximum of the  $1329\text{ cm}^{-1}$  feature in the RAIRS spectrum of Pd(111) in the presence of ethylene plotted as a function of ethylene pressure.

face as the pressure increases. This is not too difficult to understand since any defect sites not occupied during adsorption in UHV are likely to become saturated under the influence of higher pressures.

A linear regression fit to the data of Fig. 4 line shows that the line width varies substantially with pressure by  $5.3 \pm 0.4\text{ cm}^{-1}\text{ torr}^{-1}$ . It is easy to show that pressure broadening caused by collision with the gas-phase cannot account for this effect and the most generous estimate yields a maximum value of pressure broadening of  $\sim 10^{-4}\text{ cm}^{-1}\text{ torr}^{-1}$ . An alternative explanation is that it is caused by a loss of order in the ethylidyne overlayer. It is not clear whether this is formed by the apparently extra ethylidyne accommodated onto the surface suggested by the data in Fig. 3. It is likely that this would result in an increase in order of ethylidyne species adsorbed on identical sites and a corresponding sharpening of the peaks. An alternative possible explanation is that defect structures are formed on the surface in the presence of

an external pressure of ethylene due to the adsorption of ethylene between adsorbed ethylidyne species. Note that adsorbed ethylene has been detected under high external ethylene pressures using sum-frequency generation on Pt(111) [2] and will probably also occur on Pd(111). Unfortunately, any possible ethylenic species are obscured in our experiment by the preponderance of gas-phase ethylene. As noted above, experiments are now underway in which an annealed foil is substituted for the single crystal which will allow high pressures of hydrogen (~several torr) to be added to the mixture. Since this is a homonuclear molecule, it is IR invisible and will allow the surface to be examined during a catalytic reaction.

#### Acknowledgements

We gratefully acknowledge support of this work by the US Department of Energy, Division of

Chemical Sciences, Office of Basic Energy Sciences, under grant no. DE-FG02-92ER14289.

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