



Surface Science Letters

The effect of subsurface hydrogen on the adsorption of ethylene on Pd(1 1 1)

D. Stacchiola, W.T. Tysoe *

*Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee,
P.O. Box 413, Milwaukee, WI 53211, USA*

Received 3 December 2002; accepted for publication 11 June 2003

Abstract

The adsorption of ethylene on a hydrogen pre-covered Pd(1 1 1) surface was studied by reflection absorption infrared spectroscopy (RAIRS). The effect of either surface or subsurface hydrogen on the state of ethylene hybridization is explored by making use of the order–disorder transition of hydrogen on Pd(1 1 1) at low temperatures, during which the proportion of surface and subsurface hydrogen varies. The results indicate that the subsurface hydrogen is responsible for the formation of π -bonded ethylene on hydrogen-covered Pd(1 1 1).

© 2003 Elsevier B.V. All rights reserved.

Keywords: Infrared absorption spectroscopy; Chemisorption; Palladium; Alkenes; Hydrogen atom

1. Introduction

It has been shown previously that ethylene adsorbs in a di- σ -bonded configuration on clean Pd(1 1 1), but converts to π -adsorbed ethylene on a hydrogen-saturated surface [1]. Such π -bonded species adsorb less strongly than the di- σ -bonded form so that π -bonded ethylene is proposed to provide the surface species that ultimately reacts to form ethane [2–5]. A modification of the nature of the surface species by hydrogen will have a profound effect on the catalytic reaction kinetics since hydrogen will play two roles in the hydrogenation reaction, both as a reactant and as a surface

modifier. It is well known that hydrogen can both adsorb onto the surface of Pd(1 1 1) as well as diffuse into the bulk of the sample [6–9]. $\sqrt{3} \times \sqrt{3}$ R30° LEED patterns have been observed for hydrogen on Pd(1 1 1) with the unit cell containing either one or two hydrogen atoms [10,11]. An order–disorder transition has been found for these structures where the transition also affects the proportion of subsurface and surface hydrogen. Both low-energy electron diffraction analyses [10,11] and quantum calculations [12–14] reveal that hydrogen adsorbs *on* the surface in threefold hollow sites above third-layer metal atoms, and *below* the surface in octahedral sites between the first and second metal layers. It has also been demonstrated that, at a hydrogen coverage of 2/3 (where the coverages are referenced to the number of exposed palladium atoms on the surface),

* Corresponding author. Tel.: +1-414-2295222; fax: +1-414-2295036.

E-mail address: wtt@uwm.edu (W.T. Tysoe).

below the order–disorder transition temperature of 105 K, approximately 33% of the adsorbed hydrogen is present on the surface and 66% below the surface, while the distribution is random (50% surface, 50% subsurface) above the order–disorder transition temperature [10]. Since these temperatures are substantially below that at which hydrogen desorbs from the surface [4–6], the proportion of either surface or subsurface hydrogen can be adjusted merely by changing the temperature. This order–disorder transition is exploited in the following to study the form of hydrogen that affects the hybridization of adsorbed ethylene.

2. Experimental

The apparatus that was used to collect the infrared spectra has been described in detail elsewhere [15]. Briefly the sample cell used for these experiments is constructed from a 2 $\frac{3}{4}$ in. flange, six-way cross, which was modified by moving one flange by $\sim 20^\circ$ to allow infrared radiation to impinge on the sample with the optimal 80° infrared incidence angle. The cell is attached to the main chamber via a gate valve which, when closed, completely isolates the infrared cell from the ultrahigh vacuum chamber and, when open, allows sample transfer into it. Spectra are collected with Bruker Equinox spectrometer.

Ethylene coverages were measured using the so-called King and Wells method [16] using a capillary array beam source in a vacuum chamber that has been described in detail elsewhere [17].

The Pd(1 1 1) single crystal was cleaned using a standard protocol and its cleanliness monitored using Auger spectroscopy and temperature-programmed desorption collected following oxygen adsorption. The ethylene (Matheson, Research Grade) and hydrogen (Praxair, 99.9999%) were transferred to glass bottles which were attached to the gas-handling line for introduction into the vacuum chamber.

3. Results and discussion

It has been shown previously that π -bonded ethylene on Pd(1 1 1) is characterized by an infrared

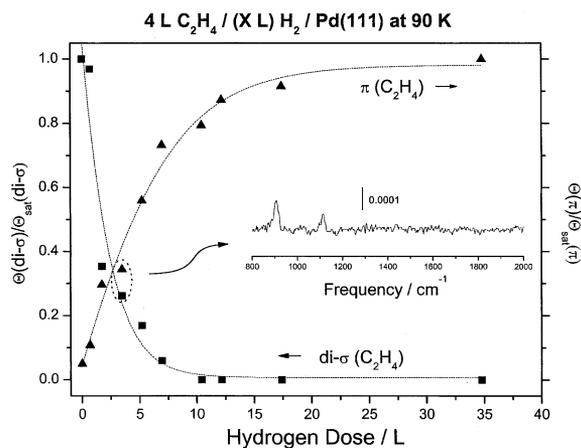


Fig. 1. Plot of the relative coverage of π - and di- σ -bonded ethylene on hydrogen-covered Pd(1 1 1) following adsorption at 90 K, as a function of hydrogen exposure. Shown as an inset is a typical RAIRS spectrum of ethylene adsorbed on a surface exposed to 4 L of hydrogen.

feature at $\sim 933\text{ cm}^{-1}$, while the di- σ -bonded species exhibits a peak at 1103 cm^{-1} and both features have been assigned to CH₂ wagging modes [1]. Shown as an inset to Fig. 1 is a typical reflection absorption infrared spectrum (RAIRS) of a saturated overlayer of ethylene on Pd(1 1 1) with an intermediate coverage of hydrogen of 0.66 monolayers (following a 3.5 L hydrogen dose, $1\text{ L} = 1 \times 10^{-6}\text{ Torr s}$). Hydrogen coverages were measured from temperature-programmed desorption (TPD) areas and calculated based on a saturation coverage of unity [6–9]. Total chemisorbed ethylene coverages were measured on clean Pd(1 1 1) at both 90 and 150 K using the so-called King and Wells method [16] where the saturation coverages were found to be identical at both temperatures and equal to 0.43 ± 0.03 (where coverages are referenced to the number of exposed palladium atoms on the (1 1 1) surface), in excellent agreement with previous measurements [18]. The ethylene coverage on hydrogen-saturated Pd(1 1 1) was also found to be the same at 90 and 150 K but slightly lower than the coverage on the clean surface at 0.23 ± 0.04 monolayers. The hydrogen signal was also monitored during these experiments and no hydrogen displacement was detected.

The data shown in Fig. 1 were collected by sequentially dosing the sample with hydrogen and

ethylene at 90 K and the infrared spectrum was also collected at 90 K. Note that this is below the order–disorder transition temperature at this hydrogen coverage. Two features are observed due to the presence of both π - and di- σ -bonded ethylene (at 933 and 1103 cm^{-1} respectively). The relative coverages of π - and di- σ -bonded ethylene are calculated assuming that they are proportional to the absorbances of the 933- and 1103- cm^{-1} features respectively. Fig. 1 reveals that the relative coverage of di- σ -bonded ethylene ($\Theta(\text{di-}\sigma)/\Theta_{\text{sat}}(\text{di-}\sigma)$, \blacksquare) decreases with increasing hydrogen exposure, while that of π -bonded ethylene ($\Theta(\pi)/\Theta_{\text{sat}}(\pi)$, \blacktriangle) increases. A shift in vibrational frequencies is also noted, where the mode for di- σ -bonded ethylene shifts from 1103 cm^{-1} on the clean surface to 1120 cm^{-1} at a hydrogen coverage of ~ 0.6 monolayers. The vibrational frequencies due to π -bonded ethylene shift from 933 cm^{-1} on the hydrogen-saturated surface to a value of 907 cm^{-1} when the hydrogen coverage has decreased to 0.35 monolayers. The data for the relative coverage of π -bonded ethylene, $\Theta(\pi)/\Theta_{\text{sat}}(\pi)$, from Fig. 1 are also plotted versus hydrogen coverage in Fig. 2 (\blacktriangle).

A second series of experiments was performed in which hydrogen was adsorbed onto Pd(111) at 90 K, the sample was then warmed to 150 K, held at this temperature, saturated with ethylene, and the infrared spectrum collected at a sample temperature of 150 K. The resulting relative coverages of π -bonded ethylene ($\Theta(\pi)/\Theta_{\text{sat}}(\pi)$), again measured from the absorbance of the 933- cm^{-1} feature, are also plotted versus hydrogen coverage in Fig. 2 (∇). It is observed in the data of Fig. 2 that adsorption of ethylene on hydrogen-pre-covered Pd(111) at 150 K results in the formation of substantially less π -bonded ethylene than adsorption at 90 K for hydrogen coverages greater than 0.5. Since, in general, the amount of subsurface hydrogen also decreases as the sample is heated [10], this suggests that subsurface hydrogen is primarily responsible for causing adsorbed ethylene to rehybridize. In order to discover if there is any correlation between the coverage of π -bonded ethylene and the amount of subsurface hydrogen, the coverage of π -bonded ethylene is written as

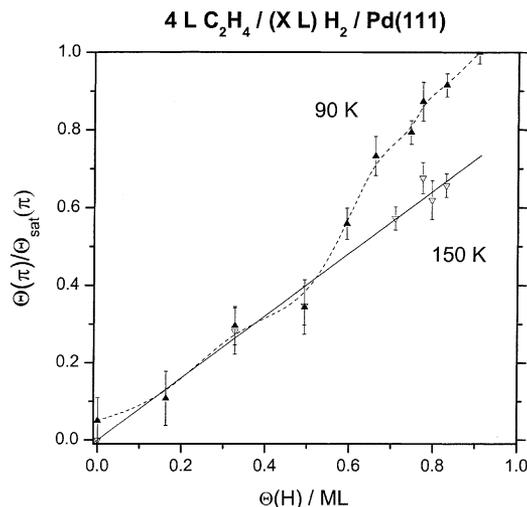


Fig. 2. Plot of the relative coverage of π -bonded ethylene on Pd(111) versus hydrogen coverage following (a) sequential adsorption of hydrogen and ethylene at 90 K where the infrared spectrum was recorded at 90 K (\blacktriangle), (b) adsorption of hydrogen on Pd(111) at 90 K, warming to 150 K followed by adsorption of ethylene and recording of the infrared spectrum, also at 150 K (∇).

$$\Theta(\text{C}_2\text{H}_4(\pi)) = A\Theta_{\text{H}}^{\text{surf}} + B\Theta_{\text{H}}^{\text{sub}} \quad (1)$$

where $\Theta(\text{C}_2\text{H}_4(\pi))$ is the coverage of π -bonded ethylene and Θ_{H} refers to the coverage of different types of hydrogen. For the data with a hydrogen coverage of 2/3, at 90 K (Fig. 2), $\Theta(\text{C}_2\text{H}_4(\pi)) = 0.73 \pm 0.03$ (Fig. 2), $\Theta_{\text{H}}^{\text{surf}} = 0.22$ and $\Theta_{\text{H}}^{\text{sub}} = 0.44$, and at 150 K, $\Theta(\text{C}_2\text{H}_4(\pi)) = 0.54 \pm 0.03$ (Fig. 2), $\Theta_{\text{H}}^{\text{surf}} = 0.33$ and $\Theta_{\text{H}}^{\text{sub}} = 0.33$ [10]. Note that the total ethylene coverage is identical at these two temperatures. Solving Eq. (1) with these values leads to $A/(\Theta_{\text{sat}}(\text{C}_2\text{H}_4(\pi))) = 0.0 \pm 0.2$ and $B/(\Theta_{\text{sat}}(\text{C}_2\text{H}_4(\pi))) = 1.7 \pm 0.2$, which implies that surface hydrogen appears to have little influence on the ethylene hybridization and that the subsurface hydrogen is primarily responsible for this effect. It should be mentioned that the proportion of surface and subsurface hydrogen has been measured [10,11] and calculated [10,12–14] on clean Pd(111), and it is conceivable that subsequently adsorbing ethylene onto this surface could influence the location of the hydrogen. In this case, however, it is unlikely that there would be such a

good correlation between the subsurface hydrogen and π -bonded ethylene coverages.

It is evident from the data of Fig. 2 that, when the hydrogen coverage is lower than ~ 0.5 monolayers, having annealed the sample from 90 to 150 K has little effect on the π -bonded ethylene coverage. It has been shown previously that the order–disorder transition temperature varies with hydrogen coverage [10]. In particular, for hydrogen coverages lower than ~ 0.55 , this temperature is always lower than 90 K so that annealing the surface to 150 K will have no effect on the proportion of surface and subsurface hydrogen. The order–disorder transition temperature exceeds 90 K only for hydrogen coverages above ~ 0.55 , and reaches a maximum value of ~ 105 K at $\Theta_{\text{H}} = 2/3$.

It is evident from the data of Fig. 2 and the values of B obtained from Eq. (1) that the effect of subsurface hydrogen is local and that only those ethylene molecules that adsorb on sites with subsurface hydrogen are π -bonded, while the remainder are di- σ -bonded. The outer surface of the palladium undergoes some geometry change following hydrogen adsorption, where the surface layer expands by ~ 0.06 Å when the hydride is formed [11,14]. Such a small change in surface morphology is unlikely to have such a drastic effect on the ethylene adsorption geometry. The degree of ethylene hybridization seems to be more closely related to the shift in energy of the metal d-band electrons [19]. Both RAIRS [1] and near-edge X-ray absorption fine structure (NEXAFS) measurements [19] show that ethylene is less rehybridized on Pd(111) than on Pt(111) and Ni(111), where the carbon–carbon bond lengths measured by NEXAFS are 1.34 Å on Pd(111) [19], 1.49 Å on Pt(111) [20], and 1.47 Å on Ni(111) from HREELS [20]. The only detailed structural determination of ethylene adsorbed on transition-metal surfaces has been a diffuse low-energy electron diffraction (LEED) investigation of a disordered overlayer of ethylene on Pt(111) [21] where asymmetrical bonding of di- σ -bonded ethylene was found on a combination of threefold hollow fcc and hcp sites. The π bonding orbital of ethylene lies ~ 5.2 eV below the Fermi level and is stabilized by ~ 1 eV due to bonding with the surface, while NEXAFS data show a π^* feature lo-

cated at about 1.2 eV above the Fermi level [19]. Since NEXAFS only probes the unoccupied portion of this state, the actual π^* location may be closer to the Fermi level than this. These observations are consistent with a synergistic bonding model with both π -donation to the metal surface and back-donation into π^* orbitals. The proximity of the π^* orbital to the Fermi level and the fact that palladium has an almost filled d-shell would suggest that a substantial contribution to ethylene bonding to the surface is via back-donation into the vacant π^* orbital of ethylene. The decrease in photoemission close to the Fermi level observed for ethylene-covered Pd(111) is in accord with this view [22]. Back-donation into a π^* anti-bonding orbital results in a weakening of the carbon–carbon bond leading to rehybridization. This suggests a possible electronic explanation for the effect of subsurface hydrogen on the ethylene hybridization. The subsurface hydrogen is located in hydride-like sites so will remove electron density from the palladium, locally increasing the separation between the palladium Fermi level and the ethylene π^* orbital, leading to less back-donation, weaker bonding to the surface and less rehybridization of the ethylene.

4. Conclusions

The adsorption of ethylene is studied on hydrogen-covered Pd(111) at 90 K where the coverage of π -bonded ethylene on the surface increases with hydrogen coverage. Since both π - and di- σ -bonded species are found at intermediate hydrogen coverages this suggests that this is a local effect. Adsorbing hydrogen and ethylene at 150 K causes the coverage of π -bonded ethylene on the surface to decrease. This decrease correlates with a change in the relative proportions of surface and subsurface hydrogen, implying that π -bonded ethylene species on the surface are formed on sites containing subsurface hydrogen. No difference is found in the proportion of π -bonded species on the surface at 90 and 150 K for hydrogen coverages lower than ~ 0.5 monolayers. In this case, the order–disorder transition temperature is lower than 90 K so that no change in the relative

surface/subsurface populations are caused by annealing to 150 K.

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 number DE-FG02-92ER14289.

References

- [1] D. Stacchiola, L. Burkholder, W.T. Tysoe, Surf. Sci. 511 (2002) 215.
- [2] P.S. Cremer, X. Su, R. Shen, G.A. Somorjai, J. Am. Chem. Soc. 118 (1996) 2942.
- [3] D. Stacchiola, S. Azad, L. Burkholder, W.T. Tysoe, J. Phys. Chem. 105 (2001) 11233.
- [4] Sh. Shaikhutdinov, M. Heemeier, M. Bäumer, T. Lear, D. Lennon, R.J. Oldman, S.D. Jackson, H.J. Freund, J. Catal. 200 (2001) 330.
- [5] Sh. Shaikhutdinov, M. Frank, M. Bäumer, S.D. Jackson, R.J. Oldman, J.C. Hemminger, H.J. Freund, Catal. Lett. 80 (2002) 115.
- [6] H. Conrad, G. Ertl, E.E. Latta, Surf. Sci. 41 (1974) 435.
- [7] W. Eberhardt, F. Greuter, E.W. Plummer, Phys. Rev. Lett. 46 (1981) 1085.
- [8] W. Eberhardt, S.G. Louie, E.W. Plummer, Phys. Rev. B 28 (1983) 465.
- [9] G.D. Kubiak, R.H. Stulen, J. Vac. Sci. Technol. A 4 (1986) 1427.
- [10] T.E. Felter, S.M. Foiles, M.S. Daw, R.H. Stulen, Surf. Sci. 171 (1986) L379.
- [11] T.E. Felter, E.C. Sowa, M.A. Van Hove, Phys. Rev. B 40 (1989) 891.
- [12] D. Faraís, P. Schilbe, M. Patting, K.-H. Riedr, J. Chem. Phys. 110 (1999) 559.
- [13] W. Dong, V. Ledentu, Ph. Sautet, A. Eichler, J. Hafner, Surf. Sci. 411 (1998) 123.
- [14] M.S. Daw, S.M. Foiles, Phys. Rev. B 35 (1987) 2128.
- [15] G. Wu, M. Kaltchev, W.T. Tysoe, Surf. Rev. Lett. 6 (1999) 13.
- [16] D.A. King, M.G. Wells, Proc. Roy. Soc. (London) A 399 (1974) 245.
- [17] D. Stacchiola, G. Wu, M. Kaltchev, W.T. Tysoe, J. Chem. Phys. 115 (2001) 3315.
- [18] L.P. Wang, W.T. Tysoe, R.M. Ormerod, R.M. Lambert, H. Hoffmann, F. Zaera, J. Phys. Chem. 94 (1990) 4236.
- [19] Q. Ge, M. Neurock, Chem. Phys. Lett. 358 (2002) 377.
- [20] H. Ibach, S.J. Lehwald, J. Vac. Sci. Technol. 18 (1981) 625.
- [21] R. Döll, C.A. Gerken, M.A. Van Hove, G.A. Somorjai, Surf. Sci. 374 (1997) 151.
- [22] J. Stöhr, F. Sette, A.L. Johnson, Phys. Rev. Lett. 53 (1984) 1684.