Title
ON THE ABSOLUTE COVERAGE OF ETHYLENE ON Pt(111) SINGLE CRYSTAL SURFACES

Permalink
https://escholarship.org/uc/item/7560q0kw

Author
Tysoe, W.T.

Publication Date
1983-12-01
ON THE ABSOLUTE COVERAGE OF ETHYLENE ON Pt(111) SINGLE CRYSTAL SURFACES

W.T. Tysoe, F. Zaera, S.M. Davis, and G.A. Somorjai

December 1983

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
ON THE ABSOLUTE COVERAGE OF ETHYLENE ON Pt(111) SINGLE CRYSTAL SURFACES

By W. T. Tysoe, F. Zaera, S. M. Davis and G. A. Somorjai

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and
Department of Chemistry, University of California
Berkeley, California 94720

ABSTRACT

The absolute saturation coverage of ethylene on Pt(111) surfaces have been determined by using four independent techniques. XPS, AES, H₂ TDS, and a ¹⁴C radiotracer technique, all suggest a value of θsat = 0.25.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.
Introduction.

Although the absolute coverage of adsorbed layers on surfaces is an important parameter for catalytic studies, very few techniques are available for its measurement. If single crystals are used as substrates, and the adsorbate orders on the surface, perhaps the most common way of estimating these coverages is the use of low energy electron diffraction (LEED). In this regard, the (2x2) LEED pattern arising from ethylene adsorption on Pt(111) surfaces at room temperature suggests that the saturation coverage in this case is a quarter of a monolayer [1-3]. However, Bonzel et al. [4,5] have recently measured the amount of carbon on the surface using X-ray photoelectron spectroscopy (XPS), and, by comparing with a CO saturated surface, reported a ethylene saturation coverage of $\theta_{\text{sat}}=0.5$. They then explained the LEED results as a superposition of three (2x1) domains with different orientations, rather than just one (2x2) superstructure.

In the present work we use XPS in a similar way as reported by Bonzel's group to estimate the saturation ethylene coverage on a platinum foil at room temperature. We find, in contrast, that the initial saturation coverage is closer to $\theta_{\text{sat}}=0.25$ than to $\theta_{\text{sat}}=0.5$, but due to the long data acquisition, additional carbon is deposited on the surface. We present additional information corroborating these results, viz., Auger electron spectroscopy (AES), temperature programmed desorption (TPD) and $^{14}$C decay data.

XPS measurements.

The XPS experiments were performed in an ultra-high vacuum (UHV) chamber described in detail elsewhere [6], equipped with a X-ray gun and double pass cylindrical mirror analyzer for AES and XPS. The base pressure was
always better than $1 \times 10^{-9}$ torr., but increased slightly after exposing the platinum foil to ethylene. XPS spectra for both ethylene and CO saturated surfaces were recorded. The C 1s peak for each adsorbate were obtained at two resolutions: 0.3 and 1.1 V (pass energies of 40 and 160 V, respectively). These are shown in fig. 1. The high resolution spectra required long data acquisition times (a couple of hours), and we found that additional carbon deposited on the surface. Low resolution spectra (10 minutes acquisition time) were obtained and corroborated this; they were used to estimate the amount of carbon on the surface in both cases. The results gave area ratios (normalized to the same ordinates) of $A_{\text{ethylene}}/A_{\text{CO}} = 0.93$ for the low resolution spectra, and $A_{\text{ethylene}}/A_{\text{CO}} = 1.24$ for the high resolution ones. Further confirmation of the increase in amount of carbon on the surface with time for ethylene adsorption was obtained using AES.

Fig. 2 shows typical Auger spectra for saturation CO and ethylene. It is worth noticing the different shapes of the carbon 273 eV peak for the two cases. The $C(273eV)/Pt(237eV)$ peak height ratio ($R_{\text{AES}}$) were used to monitor surface carbon. The results are as follow: for saturation CO, $R_{\text{AES}} = 0.54$, and saturation ethylene $R_{\text{AES}} = 0.63$. However, after obtaining the high resolution ethylene XPS spectrum, $R_{\text{AES}} = 2.48$. This shows that, using both the C 1s XPS peak area ratios and the Auger carbon signal, the amount of carbon on the foil surface after CO and ethylene saturation at room temperature are identical to within 10%, before the surface becomes further contaminated. If it is assumed for CO $\Theta_{\text{sat}} = 0.5$, this implies that ethylene saturates at a coverage of 0.25.

Other experiments.

To corroborate the value for ethylene saturation at 1/4 monolayer on
Pt(111), a series of independent experiments were carried out in a second UHV chamber, also described in detail elsewhere [7]. An absolute measurement of surface carbon was carried out using a \(^{14}\text{C}\) radiotracer technique. The carbon auger signal from ethylene was also compared with saturation CO in this chamber. Finally, the \(\text{H}_2\) TDS yield was identical when decomposing chemisorbed ethylene and when desorbing preadsorbed molecular \(\text{H}_2\).

a) Radiotracer technique.

Radiotracer experiments were carried out using a solid state detector for measuring the \(\beta\) decay of \(^{14}\text{C}\) labeled compounds. The experimental set up and the calibration procedure have been extensively described previously [8,9]. Isotherms obtained for \(^{14}\text{C}\)-ethylene chemisorption on Pt(111) at 330-570 K are shown in fig. 3. At temperatures below 450 K, the initial sticking coefficient was \(s_0=0.9\pm0.2\), saturating at \(C_s=4\times10^{14} \text{ molec/cm}^2\) [9]. This corresponds to \(\theta_{\text{sat}}=0.27\), consistent with the proposed coverage by LEED.

b) AES measurements.

Carbon Auger signals were monitored with a retarding field analyzer, using a 10 V peak to peak modulation. The shape of the peaks were similar to those obtained using a cylindrical mirror analyzer and a foil, as shown in fig. 2, limiting the accuracy of the following measurements. For CO saturation at 150 K, \(R_{\text{AES}}=0.48\pm0.04\). This ratio was 0.50\(\pm\)0.07 for ethylene adsorbed at 150 K, and did not vary significantly as the surface was warmed to 1000 K. The electron beam was defocussed to a spot size of about 1 mm to minimize electron stimulated desorption (esd). To further confirm that there was no esd, CO TDS were obtained before and after ta-
king AES spectra. These yielded identical desorption peak areas.

Since different LEED pattern were obtained for CO adsorption, there is some uncertainty in its absolute coverage, but it certainly lies between 0.5 and 0.6 [10,11]. This then corresponds to an ethylene saturation coverage of between 0.26 and 0.31 of a monolayer, in agreement with a value of $\theta_{\text{sat}} = 1/4$.

c) Hydrogen thermal desorption.

Hydrogen thermal desorption spectra were obtained after either ethylene or molecular hydrogen adsorption at 130 K, and are shown in fig. 4. The desorptions were recorded as partial pressure of hydrogen against time, which eliminates errors due to variations in the heating rate. The $H_2$ desorption peak areas obtained were $(7.0 \pm 0.1) \times 10^{-9}$ torr·sec for ethylene, and $(8.2 \pm 0.3) \times 10^{-9}$ torr·sec for molecular hydrogen. Also from the ethylene TDS we can see that the first peak, corresponding to the transformation into ethylidyne, corresponds to $25 \pm 2\%$ of the total area, an improvement over the previously reported value of $33\%$ [12]. Then, using the reported hydrogen saturation coverage on Pt(111) of unity [13,14], a value of $\theta_{\text{sat}} = 0.21$ is obtained for ethylene, again in agreement with results from the other techniques.

Thus, in conclusion, we believe that there is overwhelming evidence to confirm that the saturation coverage of ethylene on a Pt(111) single crystal surface is a quarter of a monolayer, as originally proposed based on LEED data [1-3].
References

Figure captions

Fig. 1 Carbon C 1s XPS spectra after room temperature saturation on a platinum foil: a) ethylene, 40 V pass energy, b) CO, 40 V pass energy, c) ethylene, 160 V pass energy, d) CO, 160 V pass energy. Vertical bars represent 1000 counts.

Fig. 2 Auger spectra of a Pt(111) single crystal surface after saturation at 150 K with ethylene (a) and CO (b). The spectra were obtained with a retarding field analyzer and 10 V modulation.

Fig. 3 Adsorption isotherms (left frame) for $^{14}$C-$^2$H$_4$ chemisorption on Pt(111) at 330-570 K. The adsorption behavior below 420 K is well described by a first order Langmuir model (right frame).

Fig. 4 Hydrogen thermal desorption spectra (amu=2) after H$_2$ (a) and C$_2$H$_4$ (b) saturation of a Pt(111) surface at 130 K. The heating rate is about 35 K/sec.
Fig. 1

X-ray Photoelectron Signal

Binding Energy (eV)

(a) XBL8312 - 6669
Fig. 2

Auger Spectra after Saturation on Pt (III)

(a) After C$_2$H$_4$ saturation
(b) After CO saturation

273 eV (C)
237 eV (Pt)
Fig. 3
Fig. 4

H₂ TDS

$\beta \sim 35 \text{ K/sec}$

320 K

319 K

502 K

From adsorbed H₂

5 x 10⁻¹⁰ Torr

645 K

From adsorbed C₂H₄

Time
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.