

# Structural, Kinetic, and Reactive Properties of the Palladium(111)-Ethylene System

W. T. Tysoe,<sup>†</sup> G. L. Nyberg,<sup>†</sup> and R. M. Lambert\*

Department of Physical Chemistry, University of Cambridge, Cambridge CB2 1EP, England  
(Received: December 28, 1983)

The low-temperature phase formed by ethylene on Pd(111) has been characterized by angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) and molecular beam measurements. Chemisorption occurs with an initial sticking probability of 0.8 to yield a  $\pi$ -adsorbed ethylenic species with its C-C axis essentially parallel to the metal surface; this species requires two adjacent sites for chemisorption and at saturation its fractional coverage is  $\sim 0.3$ . When the temperature was raised molecular beam and temperature programmed desorption data indicate that dehydrogenation, self-hydrogenation, and the formation of C<sub>4</sub> and C<sub>6</sub> products all take place.

## 1. Introduction

Of all the platinum metals, palladium is generally the most effective catalyst for the heterogeneous selective hydrogenation of acetylenes and diolefins.<sup>1</sup> The identity and reactivity of hydrocarbon intermediates on palladium surfaces are therefore of considerable interest and have been the subject of a number of recent investigations in which physical techniques were employed in conjunction with single-crystal substrates. Gates and Kesmodel used angle-resolved electron energy loss spectroscopy (EELS) to characterize the room-temperature<sup>2</sup> and low-temperature<sup>3</sup> phases formed by ethylene on Pd(111). They concluded that the dominant surface species at room temperature is ethylidyne (CH<sub>3</sub>-C≡) with the C-C axis perpendicular to the metal surface; the low-temperature EEL spectra were interpreted in terms of an essentially undistorted  $\pi$ -chemisorbed molecule with the C-C axis somewhat tilted out of the surface plane (C<sub>s</sub> symmetry). Demuth's angle-integrated UP spectra<sup>4</sup> also indicate that the low-temperature phase consists of essentially ethylenic species but provide no information regarding molecular orientation. Ethylidyne has also been proposed as the species which results from room-temperature chemisorption of ethylene on Pt(111)—the evidence coming from low-energy electron diffraction (LEED) intensity analyses<sup>5,6</sup> and EEL spectroscopy.<sup>7</sup> However, alternative complexes have been proposed for this same Pt surface, for example, ethylidene<sup>8,9</sup> and a multiply bonded CH-CH<sub>2</sub> species.<sup>10,11</sup> Nevertheless, comparisons with the vibrational spectrum of a cobalt-ethylidyne complex<sup>12</sup> support the view that chemisorbed ethylidyne is the dominant room-temperature surface species on the group 8A metals. The recent ARUPS results of Lloyd and Netzer<sup>22</sup> support this conclusion for the particular case of C<sub>2</sub>H<sub>4</sub> on Pd(111) at 300 K. Ethylene adsorption at low temperatures (100-150 K) has previously been studied by ARUPS on Ni(100),<sup>25</sup> Pd(100),<sup>26</sup> and Pt(111).<sup>27</sup> In each case a nondissociated, ethylene-like molecule was indicated. However, the derived orientation of the C-C axis with respect to the substrate was parallel on Pt(111) but tilted on Pd(100).

Accordingly, in the present work the adsorption kinetics and bonding geometry of the low-temperature ethylene phase on Pd(111) have been investigated by a molecular beam technique, and, for the first time, by angle-resolved UP spectroscopy. The results suggest that the low-temperature phase consists of ethylenic species with the C-C axis essentially parallel to the surface. The reactive properties of the chemisorbed layer are investigated as a function of temperature by temperature programmed desorption and by molecular beam measurements. Decomposition, desorption, self-hydrogenation, and the formation of C<sub>4</sub> and C<sub>6</sub> product species are all observed. The detection of C<sub>4</sub> and C<sub>6</sub> products is of interest in relation to very recent results of Gentle and Muettterties<sup>13</sup> and our own earlier work on the Pd(111)-C<sub>2</sub>H<sub>2</sub> system.<sup>14,15</sup>

## 2. Experimental Section

Two sets of ultrahigh vacuum apparatus were used; these have been described in detail elsewhere,<sup>16,17</sup> ARUP spectra were taken with a VG Scientific ADES 400 instrument. Kinetic studies were carried out with an effusive molecular beam source based on a capillary array or with a single capillary effusive source located 0.5 cm away from the crystal surface which was itself 1.5 cm from the ionizer of a quadrupole mass spectrometer.<sup>15</sup> Both chambers contained the usual facilities for specimen cleaning and LEED/Auger analysis. Spectroscopic grade ethylene was used without further purification.

## 3. Results

**3.1. Molecular Beam Measurements: Uptake Kinetics and Surface Reactions.** Figure 1A shows a typical pressure vs. time trace obtained with the capillary array source when the crystal at 175 K was moved in the molecular beam. Such data can readily be used to deduce the variation of relative sticking probability with relative coverage, but absolute values cannot be extracted in the absence of some independent calibration for coverage. No ordered surface phases were detected, so that LEED could not provide this information directly. However, LEED overlayer patterns are developed by the Pd(111)-acetylene system<sup>15</sup> which can therefore be used to provide a calibration for the present case. The only assumption necessary is that the fluxes of ethylene and acetylene are the same for a given source pressure. The results of this procedure are as follows: initial sticking probability at 175 K, 0.8; saturation coverage at 175 K,  $\sim 0.33$ . (The latter figure is referred to the number density of Pd atoms in the (111) plane.) From these data one may construct a plot of sticking probability as a function of surface coverage ( $\theta$ ). This is illustrated in Figure 1B from which it can be seen that the system exhibits adsorption

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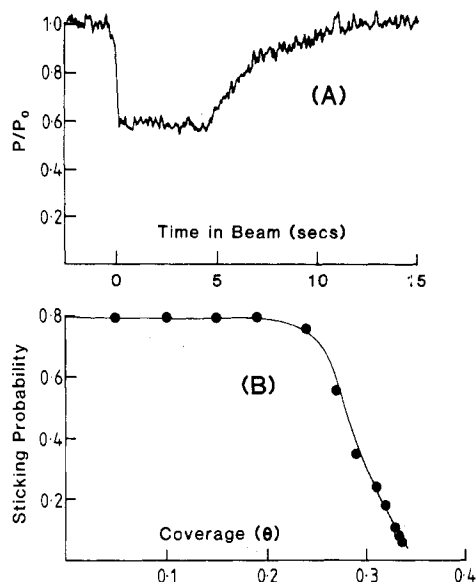
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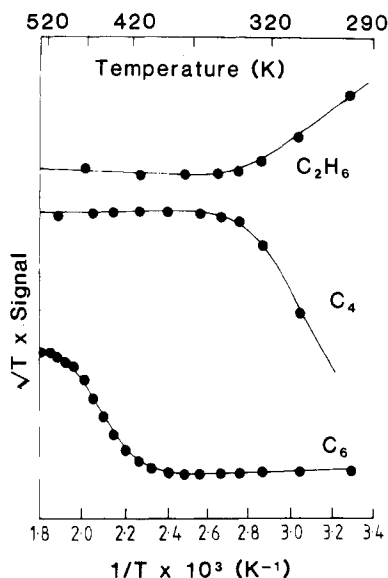
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<sup>†</sup> Building 62, Lawrence Berkeley Laboratory, University of California at Berkeley, Berkeley, CA 94720.

\*Physical Chemistry Department, La Trobe University, Bundoora, Victoria, Australia, 3083.



**Figure 1.** (A) Scattered gas pressure as a function of sample time in beam flux (capillary array) for ethylene on Pd(111) at 175 K. (B) Sticking probability as a function of coverage derived from the data in A.

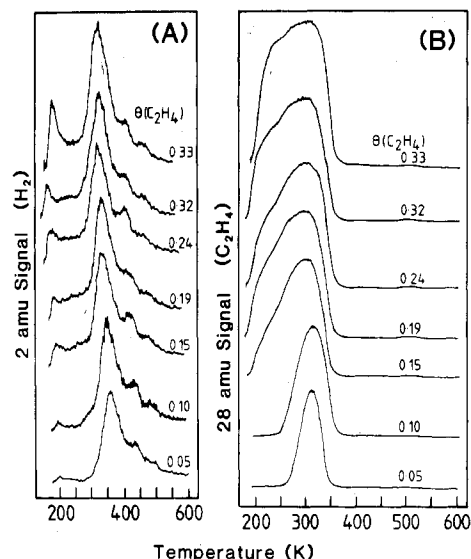


**Figure 2.** Reactive scattering of ethylene from Pd(111) (single capillary). Product fluxes as a function of temperature.

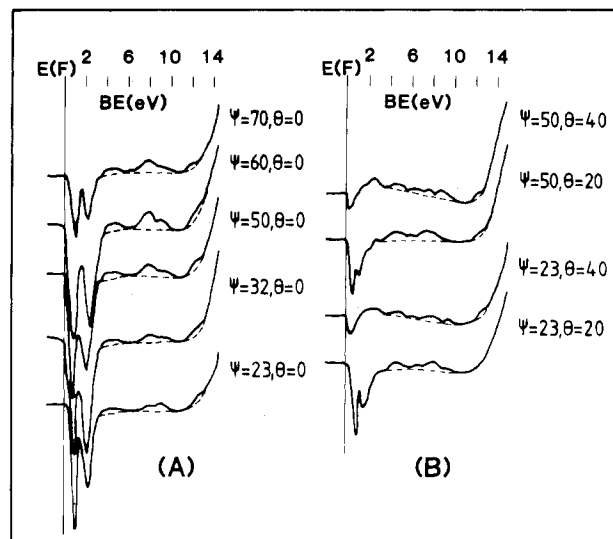
kinetics which are strongly influenced by the intervention of "precursor state" which mediates the act of chemisorption.

Corresponding measurements at 300 K could not be carried out because significant reactive scattering occurs under such conditions. Figure 2 in fact shows the mass spectrometrically detected fluxes of product species as a function of crystal temperature ( $T^{1/2} \times \text{signal}$  is proportional to flux). Ethane is observed (30 amu) along with higher molecular mass ( $C_4$ ,  $C_6$ ) products. Note that the  $C_4$  signal is not merely the result of mass spectrometer fragmentation of the  $C_6$  species and that appreciable self-hydrogenation of ethylene occurs at room temperature.

**3.2. Temperature Programmed Desorption.** Figure 3, A and B, shows the TPD spectra obtained with a heating rate of 20 K  $s^{-1}$  after subjecting the clean surface to varying doses of ethylene at 175 K. Only two desorbing species were detected:  $H_2$  (2 amu) and  $C_2H_4$  itself (26, 28 amu). No signals corresponding to ethane or higher molecular mass products were seen under these conditions. The low coverage  $C_2H_4$  spectrum consists of a single peak at  $\sim 300$  K which evolves to lower temperatures with increasing coverage. The partially resolved low-temperature feature which first appears when the ethylene coverage reaches about half its



**Figure 3.** Temperature programmed desorption spectra as a function of ethylene coverage after dosing at 175 K: (A)  $H_2$  yield; (B) ethylene desorption.



**Figure 4.** He I UP difference spectra as a function of photon angle of incidence ( $\psi$ ): (A) normal emission ( $\theta = 0$ ); (B) off-normal emission.

**TABLE I:** Percentage Hydrogen Yield from Low-Temperature Ethylene Phase as a Function of Initial Coverage

$\theta(C_2H_4)$	0.05	0.10	0.15	0.19	0.24	0.32
% ( $H_2$ )	8.6	6.9	4.0	4.0	4.0	4.0

<sup>a</sup> MS calibrated for  $H_2$  and  $C_2H_4$ .

saturation values may be the result of repulsive interactions between nearest-neighbor molecules. If this is so, the nonappearance of ordered phases at around this coverage presumably reflects limited adsorbate mobility at low temperature. An Arrhenius plot of the data for  $\theta = 0.05$  yields an activation energy to desorption of  $\sim 54$  kJ/mol; substitution of this value in the first-order desorption equation<sup>18</sup> yields a value of  $\sim 3 \times 10^9 s^{-1}$  for the preexponential factor. At high coverages the  $H_2$  spectra show two clearly resolved features and two partially resolved subsidiary features above 400 K; Table I shows that when the low-temperature phase is heated, most of the ethylene desorbs without decomposition. If this decomposition corresponds to ethylidyne formation, then even at the lowest coverage ( $\theta = 0.05$ ) only  $\sim 16\%$  of the original overlayer yields ethylidyne under the conditions of such an experiment. Hydrogen was the *only* detectable desorption product if ethylene dosing was carried out at  $\sim 300$  K, implying that an efficient reactive removal mechanism for ethylene

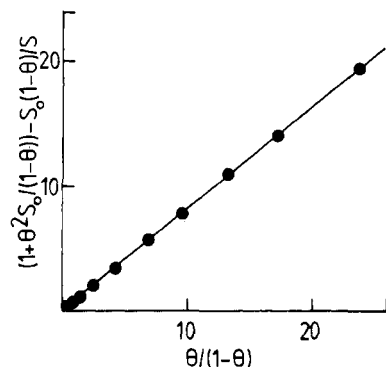


Figure 5. Pd(111)-C<sub>2</sub>H<sub>4</sub> at 175 K. Adsorption kinetics data tested against Kisliuk's "two-site" model.

TABLE II: He I UPS Peak Positions and Polarization Dependencies for the Low-Temperature Pd(111)-C<sub>2</sub>H<sub>4</sub> Phase

peak position, eV	4.4 ± 0.2	6.0 ± 0.2	7.9 ± 0.1	9.1 ± 0.1	12.0 ± 0.2
polarization dependence	Z	forbidden	Z	X, Y	?

TABLE III: He I UPS Peak Spacings for Low-Temperature Ethylene Phase Compared with Gas-Phase Ethylene

	$\pi$	$\sigma_{\text{CH}_2}$	$\sigma_{\text{CC}}$	$\sigma_{\text{CH}_2}$	$\sigma_s^*$
gaseous ethylene	2.3	1.8	1.2	3.2	
155 K phase	1.6	1.9	1.2	2.9	

operates under such conditions.

3.3. *Angle-Resolved UP Spectra.* Figure 4A shows a series of He I UP difference spectra from a surface dosed with ethylene at 155 K taken at normal emission ( $\theta = 0^\circ$ ) as a function of photon incidence angle ( $\psi$ ). Figure 4B shows a similar series of difference spectra measured at off-normal emission ( $\theta = 20^\circ, 40^\circ$ ). These data are analyzed below to yield information about the chemical identity and symmetry species of the low-temperature adsorption complex.

#### 4. Discussion

The uptake data (Figure 1) may conveniently be analyzed in terms of a model developed by Kisliuk<sup>19,20</sup> which takes explicit account of the finite "precursor state" lifetime and the number of vacant surface sites required by the chemisorbing species. In the case of "two-site" chemisorption mediated by a precursor state, the model predicts that a plot of  $\theta/(1-\theta)$  vs.  $(1+\theta^2 S_0/(1-\theta)) - S_0(1-\theta)/S$  should be linear. Such a graph is shown in Figure 5 which provides a strong indication that the molecule does in fact occupy two surface sites. (The data do not fit the corresponding "one-site" equation at all.)

Table II gives the UPS peak positions and polarization dependencies for the low-temperature ethylene-derived phase. Peak spacings are obtained from a consideration of spectra taken at both normal and off-normal emission; the peak at 6 eV below  $E_F$  appears only for  $\theta \neq 0^\circ$ . A comparison of these peak spacings with those observed for gaseous ethylene (Table III) indicates that the adsorbed species retains its olefinic character. For normal exit photoemission the final state is totally symmetric ( $A_1$ ) so that the polarization dependencies of the various photoelectron peaks may be obtained directly from their intensity variation with photon incidence angle ( $\psi$ ). Polarization dependencies derived for various plausible adsorbed ethylenic species are presented in Table IV, and comparison with the experimental  $\psi$  dependencies indicates that at low temperatures the surface species is a relatively unperturbed ethylene molecule lying with its C-C axis parallel to the surface. It can be seen from Table II that the  $\pi$  orbital in

TABLE IV: Polarization Dependencies at Normal Exit Photoemission for Possible Surface Species Exhibiting Ethylenic UP Spectra<sup>a</sup>

molecule	$\pi$	$\sigma_{\text{CH}_2}$	$\sigma_{\text{CC}}$	$\sigma_{\text{CH}_2}$	$\sigma_s^*$
flat ( $C_{2v}$ )	$a_1(z)$	$a_2(-)$	$a_1(z)$	$b_1(x)$	$b_2(y)$
side tilted ( $\sigma^{xz}$ )	$a'(x,z)$	$a''(y)$	$a'(x,z)$	$a'(x,z)$	$a''(y)$
end tilted ( $\sigma^{yz}$ )	$a'(y,z)$	$a''(x)$	$a'(y,z)$	$a''(x)$	$a'(y,z)$
twisted ( $C_2$ )	$a(z)$	$a(z)$	$a(z)$	$b(x,y)$	$b(x,y)$
on edge [CHCH] ( $C_{2v}$ )	$b_1(x)$	$b_2(y)$	$a_1(z)$	$a_1(z)$	$b_2(y)$
vinylidene [CCH <sub>2</sub> ] ( $C_{2v}$ )	$b_2(y)$	$b_1(x)$	$a_1(z)$	$b_1(x)$	$a_1(z)$

<sup>a</sup>  $x \perp \text{C-C}$ ;  $y \parallel \text{C-C}$  except for vinylidene.

the adsorbed species is shifted to somewhat higher binding energy than in the gaseous molecule: this presumably arises as a result of  $\pi$ -bonding interaction with the metal surface. The present ARUPS results would therefore appear to be in good agreement with the EELS results<sup>3</sup> in regard to both the identity of the low-temperature species and its mode of bonding. The agreement regarding molecular orientation is, however, not quite so good:  $C_{2v}$  (C-C parallel to surface) vs.  $C_s$  (C-C tilted with respect to surface plane). The proposed bonding geometry is consistent with the observations that two surface sites are necessary for chemisorption and that the fractional maximum surface coverage at low temperature is  $\sim 0.3$ .

The thermal desorption data for ethylene itself are in good agreement with the results of Gentle and Muettterties<sup>13</sup> who also observed a single weakly chemisorbed state on Pd(111) which gave a peak at  $\sim 320$  K. It is of interest to compare the kinetic parameters obtained here ( $\sim 3 \times 10^9 \text{ s}^{-1}$ ,  $\sim 54 \text{ kJ/mol}$ ) with those obtained by Zuhr and Hudson for Ni(111)-C<sub>2</sub>H<sub>4</sub> from molecular beam measurements<sup>21</sup> ( $\sim 10^{10} \text{ s}^{-1}$ ,  $\sim 50 \text{ kJ/mol}$ ). Zuhr and Hudson concluded that their values referred to a physisorbed state—possibly one located on top of a chemisorbed layer. However, the present results clearly refer to a chemisorbed layer, so that the possibility exists that ethylene may also form a weakly chemisorbed state on Ni(111) as it apparently does on Pd(111).

Heating the low-temperature olefinic phase results in most of the organic layer desorbing as ethylene. However, the thermal desorption results clearly show that a fraction of the low-temperature phase converts into another species whose ultimate fate is dehydrogenation to yield gaseous H<sub>2</sub>. In view of the EELS<sup>2</sup> and ARUPS<sup>22</sup> results for the room-temperature phase produced by C<sub>2</sub>H<sub>4</sub> on Pd(111), it is reasonable to identify this latter species with ethylidyne (CH<sub>3</sub>-C≡). This interpretation is also consistent with the appearance of the principal peak at  $\sim 350$  K in the H<sub>2</sub> TD spectrum which closely resembles the  $\sim 360$  K peak reported by Conrad et al.<sup>23</sup> for hydrogen chemisorbed on Pd(111): production of chemisorbed hydrogen is the most likely consequence of the ethylene  $\rightarrow$  ethylidyne transformation.

The decrease in hydrogen yield increasing initial coverage of ethylene is paralleled by a progressive decrease in the activation energy to ethylene desorption (Figure 3B). It therefore seems likely that the hydrogen yield is principally governed by the competition between ethylene desorption and ethylidyne formation. The remaining features in the H<sub>2</sub> TPR spectra consist of (a) subsidiary peaks at  $\sim 410$  and  $\sim 470$  K superimposed on a broad band of desorption which extends from  $\sim 400$  to  $\sim 600$  K and (b) a peak at  $\sim 180$  K which develops rapidly as the initial surface coverage approaches its saturation limit. Note that this low-temperature feature (b) becomes significant after the high-temperature peaks are essentially fully developed. The features (a) may be due to further decomposition of the ethylidyne species followed by desorption and dissolution/desorption<sup>23</sup> of hydrogen from Pd. This would account for the subsidiary peaks and the broad-band desorption. The system does not accumulate surface carbon as a result of such processes because of very efficient surface to bulk transport<sup>15</sup> of carbon at  $\sim 600$  K. The  $\sim 180$  K

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peak (b) becomes important only at high initial coverages. This suggests that it may arise from the *intramolecular* dehydrogenation of chemisorbed ethylene.

The molecular beam data (Figure 2) are qualitatively similar to those obtained for Pd(111)-C<sub>2</sub>H<sub>2</sub> by the same technique,<sup>15</sup> which suggests that dehydrogenation to acetylene<sup>13,15</sup> may precede C<sub>4</sub> and C<sub>6</sub> compound formation in the present instance. However, in the beam experiments the ethylene coverage is low, so it is unlikely that dehydrogenation proceeds intramolecularly under such conditions. With both C<sub>2</sub>H<sub>2</sub><sup>15</sup> and C<sub>2</sub>H<sub>4</sub>, C<sub>4</sub> production precedes that of C<sub>6</sub>, suggesting that the C<sub>4</sub> species is a precursor to C<sub>6</sub> formation. It is also apparent from Figure 2 that self-hydrogenation to ethane is a significant process at ~300 K. Chemisorbed hydrogen is certainly present on the surface under these conditions (section 3.2) so that this reaction is not unexpected. It seems likely that an Eley-Rideal mechanism operates between H(a) and C<sub>2</sub>H<sub>4</sub>(g) because recent measurements by Zaera and Somorjai<sup>24</sup> suggest that on Pt(111) chemisorbed ethylidyne

is *not* the precursor species for ethylene hydrogenation. In the present case, such behavior would also be consistent with the observation that H<sub>2</sub> is the only product observed in thermal desorption after dosing the surface at 300 K.

## 5. Summary

At 150 K ethylene adsorbs on Pd(111) with an initial sticking probability of ~0.8 to yield a  $\pi$ -adsorbed ethylenic species with the C-C axis essentially parallel to the metal surface. Upon raising the temperature, desorption ( $E_a \sim 54$  kJ/mol) and dehydrogenation of ethylene occur competitively. The latter process (presumably) yields ethylidyne, and at high coverages a low-temperature intramolecular dehydrogenation mechanism seems to operate. Ethane formation occurs at ~300 K while reactions leading to C<sub>4</sub> and C<sub>6</sub> products set in at ~350 and ~500 K, respectively. The molecular beam data suggest that acetylene formation may precede the production of these higher mass species.

*Acknowledgment.* W.T.T. thanks the S.E.R.C. for the award of a Research Studentship. We are grateful to Johnson Matthey Ltd. for the loan of precious metals.

**Registry No.** Ethylene, 74-85-1; palladium, 7440-05-3.

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## Secondary Ion Mass Spectrometry and Electron-Stimulated Desorption as Probes of Covalently Modified TiO<sub>2</sub> and SiO<sub>2</sub> Surfaces

Todd R. Hayes and John F. Evans\*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

(Received: August 12, 1983)

TiO<sub>2</sub> and SiO<sub>2</sub> surfaces modified with covalently bound organosilanes have been examined via two mass spectrometric surface analytical techniques: secondary ion mass spectrometry and electron-stimulated desorption. Hexamethyldisilazane and hexa(methyl-*d*<sub>3</sub>)disilazane vapors were reacted with the corresponding surfaces to yield monolayer or submonolayer coverages of bound trimethylsilyl and tri(methyl-*d*<sub>3</sub>)silyl groups. A 1.0-keV Ar ion bombardment of the modified TiO<sub>2</sub> and SiO<sub>2</sub> results in the ejection of secondary ions with the formulas [(CH<sub>3</sub>)<sub>*n*</sub>Si]<sup>+</sup>, where *n* = 3, 2, 1, and 0, in addition to ions originating from the oxide lattice. Various spectral features also indicate the formation of molecular ions by seldedge recombination and/or by molecular rearrangement during static SIMS analysis. A 1.0-keV electron bombardment of modified SiO<sub>2</sub> yields the methylsilyl ion series observed in SIMS. Trimethylsilyl groups bound to TiO<sub>2</sub> are ca. 5 times more stable under electron bombardment than the SiO<sub>2</sub> system. Methylsilyl ions are produced, but no trimethylsilyl cation is detected in the case of the TiO<sub>2</sub> substrate. The dependences of the parent ion signal with primary particle dose were examined, and, in light of these and related data, plausible damage mechanisms which lead to the decrease of the surface concentration of intact trimethylsilyl groups are discussed.

## Introduction

Secondary ion mass spectrometric (SIMS) analysis of nonvolatile and condensed molecules is developing rapidly as an analytical technique. Studies of multiple layers of organic molecules adsorbed (or condensed) on solid supports<sup>1-6</sup> have demonstrated that molecular weight as well as structural information may be obtained from parent and fragment secondary ions. The analysis of polymer

surfaces<sup>7-10</sup> has shown that differences in fragmentation patterns may reflect differences in the monomeric structure of the polymer. It is important to note that these particular applications of SIMS necessitate low primary ion beam fluences, such that the secondary ion signal originates only from a statistically undamaged cross section of the surface.<sup>11</sup>

Rather than adsorbed multilayers, our interests lie in the mass spectrometric analysis of monolayer coverages of molecules covalently bonded to a surface. There have been a few SIMS studies investigating such inorganic chemisorbates as CO on Ni.<sup>12,13</sup> We

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