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Thermal Decomposition of CH_3OH Adsorbed on Pd{111}: A New Reaction Pathway Involving CH_3 Formation

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Abstract: The adsorption and subsequent decomposition of CH_3OH on Pd{111} has been examined with X-ray photoelectron spectroscopy and secondary ion mass spectrometry (SIMS) over the temperature range 110–600 K. We find that the thermal decomposition reaction pathway after adsorption at 110 K is strongly dependent on the initial CH_3OH exposure. Below the saturation CH_3OH exposure of 1.5 langmuirs the primary decomposition products are observed to be CH_{3ads}, OCH_{3ads}, and H_2O_{ads}. This chemistry suggests that the methanolic C–O bond is activated at the metal surface. These products are observed to form at temperatures as low as 125 K. For exposures above 1.5 langmuirs this decomposition pathway is no longer observed, possibly due to a site blocking effect, and molecular desorption occurs with trace decomposition. Interestingly, we find no evidence that CH_3OH adsorbed at 110 K with initial exposures below 1.5 langmuirs decomposes to CO at any temperature below the thermal desorption temperature of CO at 490 K. Finally, the SIMS ion observed at m/e 15 (CH_{3ads}) and associated with the decomposition of CH_3OH is found to persist over the rather wide temperature range 125–400 K. The unusual stability of CH_{3ads} suggested by these findings may be related to the effectiveness of Pd-based catalysts to produce CH_3OH.

Investigations of the surface chemistry of CH_3OH on transition-metal surfaces serve to enhance the understanding of CH_3OH-based catalysis[1] and to provide insight into fundamental bond making/breaking reactions involved in gas–surface reactions. In this paper we probe the adsorption and subsequent thermal decomposition of CH_3OH on Pd{111} as the temperature is increased from 110 to 600 K using secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS). The reactivity of CH_3OH on a metal is of surface chemical interest because of the three heteroatom bonds present in the molecule. It is of catalytic interest not only because its efficient production may provide an alternate fuel source but also because CH_3OH is used as a reactant in a number of catalytic processes. We have chosen to investigate the reactivity of CH_3OH on Pd{111} because of the ability of Pd to produce CH_3OH from CO to H_2[2,3] under catalytic conditions. The surface chemistry developed here describes the first observation of the activation of the methanolic C–O bond to produce a CH_{3ads} species and may have implications for the mechanism of CH_3OH production on Pd-based catalysts.

A number of previous investigations have demonstrated that the low-temperature surface chemistry of CH_3OH depends both on the metal substrate and on the temperature of adsorption. On Cu{110}[4] and Cu{111}[5] CH_3OH adsorbs at 180 K without chemical degradation. Similarly, there are no reactions observed for CH_3OH upon adsorption on Pd{111}[6] at 140 K and on Pt{111},[7] Ni{111},[8] and Al{111}[9] between 90 and 100 K. On Al{110},[10] however, electron energy loss spectroscopy (EELS) studies suggest that OCH_{3ads}(methoxide) is the primary reaction product at 140 K. On Pd{100}[11] at 77 K thermal programmed desorption (TPD) and EELS measurements also suggest that the first 20% of a monolayer adsorbs as OCH_{3ads} while the remainer is adsorbed as CH_3OH. This chemistry implies that the methanolic O–H bond is somehow activated both by the presence of the metallic substrate and by the temperature of adsorption. On Ru{001}[12] at 80 K, EELS and TPD studies indicate that C_{ads}, O_{ads}, and OCH_{3ads} are formed upon adsorption. This more dramatic chemistry implies that the metallic substrate is activating the methanolic C–O bond. Finally, it is noteworthy that the formation of OCH_{3ads} is promoted on Cu,[4] Pt,[7] Ru,[13] Ni,[14] and Pd[6,15] metal surfaces when predosed with several langmuirs of O_2 at 300 K. In this reaction, it is believed that the chemisorbed O atom provides a hydrogen abstraction site to produce the CH_3O species.

The thermal decomposition pathway for CH_3OH may be quite straightforward, such as for the Cu{111}[9] surface where the molecule simply desorbs intact. Usually, however, the situation is quite complex. The EELS and TPD measurements for CH_3OH adsorption on Pd{100}[11] at 77 K reveal that there are a number of different desorption states observed as the initial exposure is changed. While the multilayer CH_3OH thermal desorption feature is observed at 142 K, a series of CO and H_2 desorption states is seen above this temperature, which suggests that more stable hydrocarbon adsorbates are present in addition to CH_3OH_{ads}. The TPD spectra observed for CH_3OH adsorption on Pd{111}[16] at 170 K are consistent with the presence of a similar (desorption) reaction pathway. In addition to the CH_3OH molecular desorption feature at 200 K on Pd{111} there is an H_2 desorption peak at 330 K and a CO desorption peak at 490 K. On Pt{111},[7] Ni{111},[8] Ni{110},[17] and Al{111},[9] EELS experiments suggest that CH_3OH which is molecularly adsorbed at 100 K decomposes to OCH_{3ads} between 140 and 200 K on the clean surface. Finally, on Ni{110},[18–20] the CH_3O_{ads} as well as species with COH stoichiometry have been observed during thermal decomposition at temperatures of 170 and 240 K, respectively.

As is evident from the above discussion the presence of the CH_3O adsorbate, which denotes methanolic O–H bond activation, is well documented. There is some dispute as to whether decomposition can occur at the methanolic C–O bond. Activation at this bond has been suggested previously on Ru{001}[12] from TPD measurements which indicate that H_2O and CH_4 are desorbed from the surface. A subsequent study[21] on Ru and Rh, however, using pulsed field desorption mass spectrometry, was unable to confirm this hypothesis. Activation of the methanolic C–O bond

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has also been suggested to occur on a Ni foil under a high flux of CH_3OH.[22] A subsequent investigation[23] on Ni{111} was unable to detect isotopic scrambling between $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$, suggesting that the methanolic CO bond remains intact. Thus, at this stage, both the decomposition pathways for chemisorbed CH_3OH as well as the general principles necessary for understanding its surface reactivity remain quite muddled.

We have recently reported[24] XPS and SIMS data that suggest that CH_3OH adsorbed at 110 K on clean Pd{111} dissociates upon heating at both the C–O and O–H bond after an initial exposure of 1.5 langmuirs. In this work, we expand that discussion by examining the nature of the initial CH_3OH layer and the formation of carbon-containing surface fragments through a detailed analysis of the XPS C 1s intensity, binding energy (E_b), and peak full width at half-maximum (fwhm). The results show that the decomposition pathway of CH_3OH is strongly dependent on the magnitude of the initial CH_3OH exposures and on the rigorous exclusion of initial sources of oxygen. In combination with SIMS experiments, we provide conclusive evidence that under the conditions of an atomically clean Pd{111} surface for CH_3OH exposures of 1.5 langmuirs or less C–O bond activation is a major decomposition pathway at temperatures as low as 125 K. The initial reaction product, identified as CH_{3ads} by XPS and SIMS, appears to be an unusually stable intermediate on Pd. At higher initial exposures or when the surface is predosed with extremely low levels of O_2, the CH_3OH decomposes exclusively via a OCH_{3ads} intermediate. Interestingly, we find no evidence using XPS or SIMS for chemisorbed CO with initial exposures of 1.5 langmuirs or less at any temperature below the thermal desorption temperature of CO at 490 K. The decomposition pathways of the deuterated CH_3OH analogues have also been examined using SIMS. These experiments are exceedingly helpful in confirming the presence of CH_{3ads} and for eliminating artifacts due to possible ion-beam-induced recombination processes. In general, we have found that the decomposition mechanism of chemisorbed CH_3OH is extremely complex and critically dependent upon initial adsorption conditions as well as on the purity of the single-crystal substrate.

Experimental Section

Experiments were performed in an ultrahigh-vacuum (UHV) chamber, with a base pressure of 2×10^{-10} Torr. The details of the Leybold-Heraeus EA-11 electrostatic energy analyzer and X-ray source used for XPS studies and the Riber SIMS system have been previously described.[25] The Pd{111} crystal was cut from a boule at the Cornell Materials Preparation Laboratory. The crystal was reoriented in this laboratory by using Laue back diffraction to within ±0.5° and polished by standard crystallographic techniques. The polished crystal subsequently exhibited sharp (1 × 1) LEED spots indicative of the {111} orientation. Bulk carbon, sulfur, and phosphorus impurities were removed over the course of several weeks by cycles of the following cleaning routine. Carbon contaminants were removed by heating the crystal to 650 K for 20 min in 1×10^{-7} Torr of O_2. The remaining contaminants were removed by 3-keV, 2-μA Ar^+ ion sputtering for 5 min at room temperature. The crystal was then annealed to 1300 K to redistribute bulk contaminants to the near surface region so that they could be removed by subsequent segregation and sputtering steps. The surface cleaning routine prior to each experiment consisted of 3-keV, 2-μA Ar^+ ion sputtering for 5 min, followed by flashing to 1300 K to anneal the surface. It was necessary to flash to at least 1200 K to remove surface and subsurface O_{ads}. Finally, the crystal was precooled to 110 K and subsequently flashed to 1300 K to remove any trace CO or O impurities. The surface was checked prior to every experiment for carbon or oxygen impurities by using SIMS or XPS.

The removal and exclusion of O_2 from the sample surface is the most critical part of the sample preparation procedure. The results presented in this paper for clean Pd{111} could be obtained only by precisely following the above cleaning methods. In addition, we found that the O_2 used to remove bulk C from a new Pd crystal served as an important adventitious impurity source. For example, during the high-temperature annealing step, this O_2 source was found to desorb from the region near the heater and manipulator and redeposit on the crystal during the cooling cycle. The resulting trace O_2 surface concentration (<3% monolayer) was then sufficient to quench the methanolic C–O bond activation step. To avoid this problem, no O_2 was admitted to the UHV system during the several months over which these experiments were performed. Other attempts to observe C–O bond activation using oxygen treatments to remove surface carbon have apparently not yet been successful.[27]

The CH_3OH was distilled into an evacuated flask and was then purified by several liquid nitrogen freeze–pump–thaw cycles to remove gaseous impurities. The CD_3OH and CH_3OD were obtained from MSD Isotopes and Aldrich, respectively. The deuterated species were dehydrated and purified by using hot zeolite followed by several freeze–pump–thaw cycles. The CH_3OH in the dosing line was changed after every few days to ensure that no significant decomposition was occurring. The exposures are reported in langmuirs (1 langmuir = 1×10^{-6} Torr·s) and are taken from ionization gauge readings which are corrected by a factor of 1.9.[26]

The Ta sample holder was cooled by using liquid nitrogen flowing through a stainless steel reservoir in thermal contact with the sample holder. The minimum temperature obtained after approximately 30 min was 110 K. Sample heating was achieved by using electron bombardment from behind the crystal surface, which allowed temperatures of 1400 K to be obtained within 2 min. A chromel–alumel thermocouple was attached to the Ta sample holder just below the crystal.

The SIMS spectra were taken with ion currents ranging between 0.4 and 2.0 nA cm^{-2} to prevent significant ion beam damage to the surface. Each spectrum, scanned between m/e 0 and 220, required approximately 2 min to record. The background SIMS spectrum taken before each experiment revealed only Na^+ and K^+ signals with no Pd^+ (m/e 102, 104, 105, 106, 108, and 110) detected. The secondary ion intensities as a function of temperature were determined directly from the entire mass spectra recorded every 25 K between 110 and 300 K.

The XPS spectra were recorded by using an Al Kα X-ray anode. All binding energies, E_b, are reported relative to the Pd Fermi level which places the Pd $3d_{5/2}$ level at 335.5 eV. The fwhm for a typical C 1s peak for a single carbon species using an Al anode in our system is 1.5 eV. The spectra were collected at an angle of 42° from the surface normal unless otherwise noted. The C 1s, O_{KLL} Auger, Pd $3d_{5/2}$, and Fermi level were collected as the crystal cooled from the desired reaction temperature. All of the E_b values were reproducible to ±0.05 eV from day-to-day but are reported here to ±0.1 eV. The peak positions are determined from the center of the photoelectron intensity as recorded. Since the C 1s region for clean Pd{111} is featureless and of constant intensity, it was not necessary to subtract a background signal from the spectra.

Results and Discussion

The reactivity of CH_3OH with transition-metal surfaces has shown great sensitivity to the type of metal, surface orientation, temperature of deposition, and temperature of observation. This rich chemistry arises in part since the C–H, C–O, and O–H bond strengths are similar and are significantly weaker than many other commonly studied surface molecules. For example, the CH_3OH bonds are all approximately 4 eV, while the carbon monoxide bond strength is more than 11 eV. The standard techniques used to unravel the surface chemical reactions of CH_3OH have been EELS and TPD. While EELS is quite sensitive to several adsorbate vibrational bands, the dipole scattering cross section for many adsorbates of interest remains too low to be easily detected. Similarly, TPD is insensitive to the presence of any number of reactions that can occur before the observed molecule desorbs from the surface. In this section, we examine the decomposition pathway for CH_3OH in a regime that is between that of the initial adsorption species observed by using EELS and the final desorption product observed by using TPD. Our approach is to combine the qualitative, high molecular specificity of SIMS with the quantitative, low molecular specificity of XPS to directly determine the concentration and composition of the methanolic reaction products that remain on the surface as a function of temperature.

Adsorption Pathway for CH_3OH on Pd{111} at 110 K. The first step in our analysis is to utilize XPS and SIMS to examine the clean Pd{111} surface and the Pd{111} surface exposed to CH_3OH

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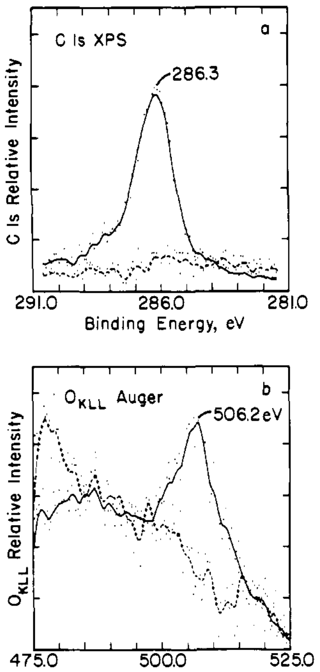

Figure 1. Carbon 1s XPS (a) and O_{KLL} Auger spectra (b) for clean Pd{111} (---) and for Pd{111} exposed to 2.5 langmuirs of CH_3OH at 110 K (—).

at temperatures below those required to initiate decomposition. With XPS, the C 1s and O 1s regions are typically employed to check for the presence of adventitious impurities. As seen from Figure 1a, the C 1s region for clean Pd{111} reveals that no carbon impurity is present as indicated by the featureless dashed base line. The O 1s region near 531 eV, however, is largely obscured by the prominent Pd $3p_{3/2}$ photoelectron line at 532 eV. As a result, the relatively weak and broad O_{KLL} Auger transition must be employed to detect oxygen-containing impurities. A typical clean background is shown by the dashed-line O_{KLL} spectra in Figure 1b. Upon exposure to 2.5 langmuirs of CH_3OH at 110 K significant features are found in both the C 1s and O_{KLL} spectra. The C 1s spectrum exhibits only one peak with an E_b value of 286.3 eV. The fwhm of 1.7 eV, which is 0.2 eV larger than the minimum fwhm for one species, suggests that two closely related carbon forms are present at this exposure. There is additional evidence presented subsequently that suggests that this increase in fwhm arises from the presence of a chemisorbed and physisorbed CH_3OH overlayer. The C 1s E_b value of 286.3 eV is a reasonable one for a carbon-containing fragment that is bound to oxygen. Previously reported values for the methanolic C 1s E_b value include 285.6 eV for CH_3OH on Fe{100}[28] at 180 K, 286.9 eV for 5 langmuirs of CH_3OH on Al foil,[29] and 286.2 eV for CH_3OH at 140 K on Cu{110}.[30] The O_{KLL} Auger intensity for CH_3OH on Pd{111} is centered about 506.0 eV. We note that while the kinetic energy of this Auger transition could be obtained only to a precision of ±0.5 eV, the C 1s to O_{KLL} intensity ratio was approximately the same throughout the experiments.

The SIMS data are complementary to the XPS results discussed above. The SIMS spectrum resulting from a 6-langmuir exposure to Pd{111} at 110 K is shown in Figure 2. This rather complex spectrum may be fully interpreted by comparison to spectra for CD_3OH and CD_3OD obtained under similar conditions. The peak at *m/e* 15 in Figure 2 is assigned to CH_3^+ on the basis of the CD_3OH spectrum shown in Figure 3, which exhibits a CD_3^+ ion at *m/e* 18. The peaks at *m/e* 18 in Figure 2 are assigned to H_2O^+ in a similar manner. The peaks at *m/e* 31 and 33 are assigned to CH_2OH^+ and CH_3OHH^+ on the basis of the CD_3OH spectrum,

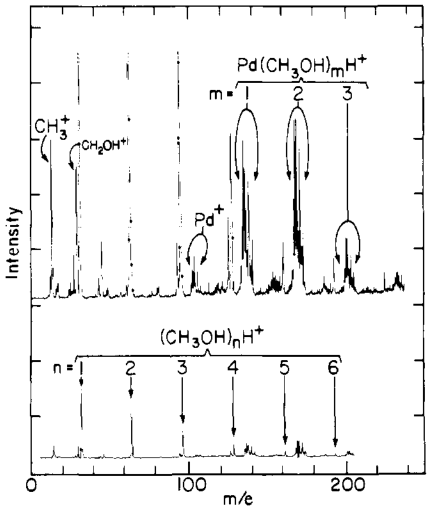

Figure 2. Positive ion SIMS spectra for Pd{111} exposed to 6 langmuirs of CH_3OH at 110 K. The spectra were recorded by using a 3-keV Ar^+ primary ion beam with a current density of 0.4 $nA\cdot cm^{-2}$. The top spectrum is shown with a 10× magnification.

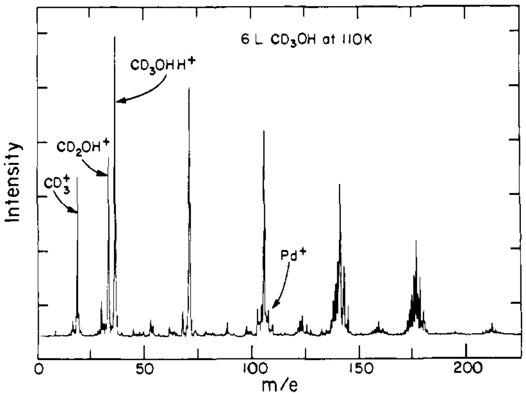

Figure 3. Positive ion SIMS spectra for Pd{111} exposed to 6 langmuirs of CD_3OH at 110 K. The spectra were recorded by using a 3-keV Ar^+ primary ion beam with a current density of 0.4 $nA\cdot cm^{-2}$.

which exhibits peaks at *m/e* 33 and 36. The CH_2OD^+ species, rather than the CH_3O^+ species, is also observed by using electron beam ionization of gaseous CH_3OD.[31] Under our experimental conditions no evidence was obtained for CH_3O^+ (*m/e* 31) or CD_3O^+ (*m/e* 34) in the positive SIMS spectra at any temperature. The ion detected at *m/e* 47 in the CH_3OH spectrum is assigned to $(CH_3)_2OH^+$, from the corresponding shifts observed in the isotopically labeled SIMS spectra. This peak is seen only in spectra where a CH_3OH multilayer exists and is attributed to the cracking of larger methanol ice clusters. Peaks assignable to $(CH_3OH)_nH^+$ *n*-mers are observed as marked in the figure. The Pd^+ isotopes are detected at *m/e* 102, 104, 105, 106, 108, and 110. An array of $Pd(CH_3OH)_mH^+$ peaks is also apparent. Adsorption of CH_3OH at 300 K produces a large increase in the Pd^+ and $PdCO^+$ ion intensities, but no evidence is found for CH_3OH_{ads} species. Thus, at 300 K, CH_3OH decomposes to form CO and H_2, which is in agreement with previous studies.[6] It is clear that little surface chemical information may be gleaned from these measurements alone. As will be seen, however, important mechanistic details are embedded in a series of SIMS spectra obtained as a function of CH_3OH exposure or surface temperature.

A more detailed inspection of the XPS and SIMS results for CH_3OH adsorption at 110 K yields a rather complex picture for even this simple experimental situation. The C 1s spectra for CH_3OH_{ads} resulting from exposures between 0.5 and 6 langmuirs are shown in Figure 4. Several trends are apparent in the figure, and each has implications for the adsorption mechanism of

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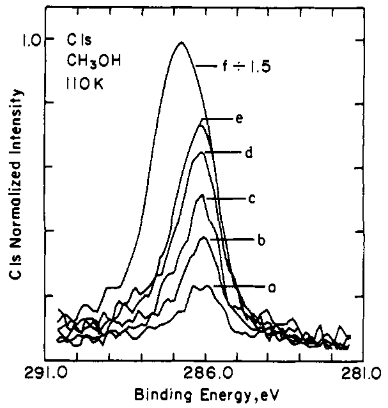

Figure 4. Carbon 1s spectra for Pd{111} exposed to (a) 0.5, (b) 1, (c) 1.5, (d) 2, (e) 2.5, and (f) 6 langmuirs of CH_3OH at 110 K. Note that curve f has been reduced in intensity by a factor of 1.5.

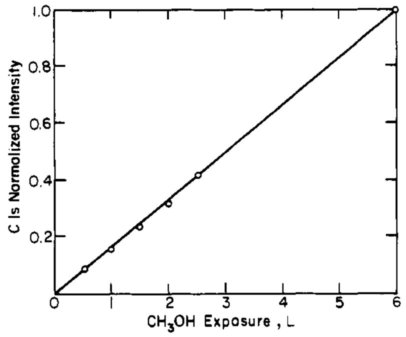

Figure 5. Relation between the XPS C 1s intensity and CH_3OH exposure at 110 K. The points are obtained from the data presented in Figure 4. The line is a linear least-squares fit to the points.

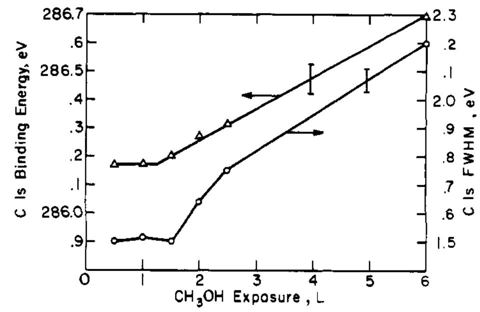

Figure 6. Relation of the C 1s E_b values and the peak fwhm with CH_3OH exposure. The C 1s E_b values (△) are plotted with ±0.1 eV resolution. The C 1s fwhm (○) is plotted with ±0.04 eV resolution. Points are taken from the C 1s spectra shown in Figure 4.

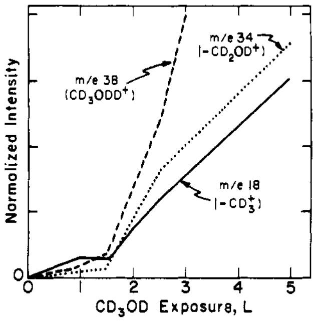

Figure 7. Selected SIMS ion intensities from Pd{111} as a function of CD_3OD exposure at 110 K. All of the ion intensities are determined from peak heights and are reported relative to the intensity of the CD_3ODD^+ ion at 110 K.

CH_3OH on Pd{111}. The plot of the C 1s intensity as a function of exposure, shown in Figure 5, simply demonstrates that the sticking coefficient at 110 K is constant throughout the adsorption. We presume at this temperature that the value of the sticking coefficient is near unity. The plot also demonstrates that a number of multilayers are produced at this temperature since the C 1s intensity continues to rise as the number of CH_3OH molecules available for adsorption exceeds that needed for one layer to form. As the exposure is increased above 6 to 50 langmuirs (not shown), the C 1s intensity continues to increase but at a slower rate, presumably due to the fact that the photoelectrons escape only from the top few layers.[32]

The behavior of the C 1s E_b value and fwhm as a function of coverage are shown in Figure 6. The most important result to be gleaned from these data is that the C 1s peak shape and position are constant with coverage up to the 1.5-langmuir exposure point. This result suggests that no significant chemical alterations are occurring during the formation of this layer. Above 1.5 langmuirs, however, the E_b value increases from 286.2 to 286.7 eV and the fwhm value increases from 1.5 to 2.2 eV. An important point implied by these trends is that the completion of the first monolayer of CH_3OH_{ads} occurs at an exposure of 1.5 langmuirs and that additional CH_3OH exposure results in the formation of a multilayer. These trends in the data are certainly consistent with the formation of multilayers of CH_3OH since their electronic environment is expected to be slightly different than that of CH_3OH in intimate contact with the metallic substrate. The feature we observe, then, is a convolution of the contribution from the first layer of adsorbed CH_3OH with subsequent condensed layers. It is interesting that at the highest exposures of 50 langmuirs the fwhm decreases again to 1.7 eV. At this coverage, apparently all of the CH_3OH molecules in the ice layer are in equivalent electronic environments and no electrons are originating from molecules in contact with the metal. Possible charging effects as well as possible changes in reference levels complicate the analysis of these chemical shifts, although we feel they are useful for providing empirical evidence for multilayer formation. Multilayer formation has also been observed to begin to form on Pd{100} at 77 K[11] between 1.5 and 2 langmuirs of CH_3OH exposure. This case is somewhat different than for Pd{111} since the initial adsorbed layer on Pd{100} is believed to have converted to OCH_{3ads}.

We have performed SIMS experiments on methanol layers produced under identical conditions using CD_3OD as a precursor. The deuterated molecule allows more direct assignment of hydrocarbon fragments which may contain a significant number of hydrogen atoms. The C_1 hydrocarbon SIMS ion intensities (CD_3^+, CD_2OD^+, and CD_3ODD^+) corroborate the proposed adsorption mechanism established from XPS measurements as a function of exposure at 110 K. As shown in Figure 7, there is a marked change in appearance at 1.5-langmuir exposure corresponding to completion of the first CH_3OH monolayer. The changes in the relative intensities of these fragment ions are rather more difficult to interpret. Below 1.5-langmuir exposure, for example, the CD_3^+ ion intensity is higher than the others. We believe this behavior arises from the cracking of CD_3OD during desorption rather than from the formation of CD_{3ads} since as seen in Figure 4 no XPS evidence is found near 284 eV for a species of this type. It is possible that the enhanced CD_3^+ signal arises since CH_3OH_{ads} bonds to the surface through the oxygen atom below saturation coverage.[17] For exposures above 1.5 langmuirs the CD_3ODD^+ ion exhibits the largest intensity, which is again consistent with the fact that multilayers are forming. Similarly the CD_3^+ and CD_2OD^+ ion signals also increase in intensity as a function of exposure. Since the XPS data indicate only the buildup of a methanol overlayer, we conclude that the increase in these signals is a result of fragmentation of CD_3OD during the primary ion impact event or on its way to the detector and is not due to the formation of new surface species. We note that even though alterations in the methanolic SIMS cracking pattern as a function of exposure complicate a simple interpretation, these changes are extremely sensitive to the electronic state of the adsorbate and thus have significant qualitative value.

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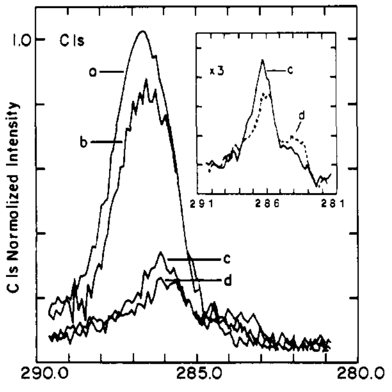

Figure 8. XPS C 1s intensity for Pd{111} exposed to 6 langmuirs of CH_3OH at 110 K (a). In the subsequent curves, the sample is heated to (b) 160, (c) 175, and (d) 275 K. Note that the E_b values corresponding to the peak intensities are 287.7 eV in (a), 286.5 eV in (b), 286.2 and 284.5 eV in (c), and 285.9 and 284.0 eV in (d). The inset displays (c) and (d) at a 3× magnification. All spectra are normalized to curve a.

Thermal Reactivity of CH_3OH_{ads} on Pd{111}. We next examine the decomposition pathway of CH_3OH after adsorption on Pd{111} at 110 K at various initial exposures. Our approach is quite similar to that detailed above for the characterization of the adsorption pathway. The XPS method is utilized to provide surface concentrations with limited chemical specificity while the SIMS analysis in combination with isotopic labeling experiments yields more detailed molecular information. The key result of our experiments is that the decomposition pathway is strongly dependent on the initial CH_3OH exposure. At 6 langmuirs and above, the molecule falls apart primarily via the familiar OCH_{3ads} surface intermediate. At initial exposures below 2 langmuirs, however, we find clear evidence for the activation of the C–O bond and the formation of a stable CH_{3ads} intermediate. In this section, then, we detail separately the spectral information for each exposure regime.

CH_3OH Exposures of 6 Langmuirs. The C 1s spectra for a 6-langmuir exposure of CH_3OH as a function of temperature, shown in Figure 8, reveal a number of interesting mechanistic points. First, the rapid decline of the C 1s intensity between 110 and 160 K is consistent with simple molecular desorption of the CH_3OH multilayer. Our data shown in Figure 8c demonstrate that after the multilayer desorption occurs, the C 1s peak splits into a doublet at 175 K. The feature with an E_b value of 286.2 eV corresponds to that of associatively adsorbed CH_3OH or OCH_{3ads}. The peak at 284.2 eV is consistent with a C_{ads} species at trace concentration on the surface. As we shall see, SIMS and XPS measurements taken at exposures of 1.5 langmuirs or below suggest that this species is CH_{3ads}. The decrease and shift in the E_b value of the high-binding-energy peak to 285.9 eV upon further heating to 273 K are attributed to the formation of OCH_{3ads}. We make this assignment since parallel studies of a Pd{111}/O precovered surface,[33] known to produce a pure OCH_{3ads} overlayer,[6] also yield C 1s XPS spectra characterized by a single peak with an E_b value of 285.9 eV. Note that the peak at 284.2 eV increases in intensity at 275 K, suggesting some additional formation of CH_{3ads}.

The analysis of the SIMS spectra for a 6-langmuir CH_3OH exposure as a function of temperature is in agreement with the XPS-based interpretation. In our experiments, illustrated by the data shown in Figure 9, the intensity of various SIMS cluster ions is plotted as the temperature is increased from 110 to 300 K. These peaks are attributed to CH_3OHH^+, CH_2OH^+, CH_3^+, and H_2O^+ as indicated. The intensity of the CH_3OH-related ions, CH_3OHH^+ and CH_2OH^+, decreases rapidly to zero as the surface temperature approaches 175 K. This result is consistent with the simple thermal desorption of the adsorbed multilayer as implied by the XPS data in Figure 8 and with previous EELS[6] and TPD[16] experiments.

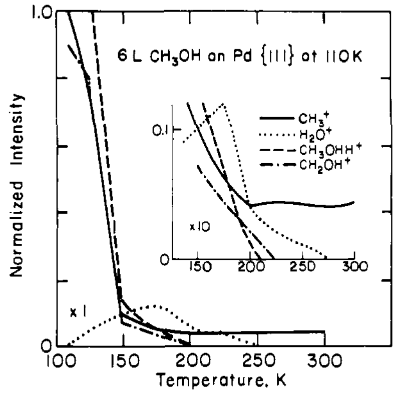

Figure 9. Various SIMS ion intensities as a function of temperature for Pd{111} exposed to 6 langmuirs of CH_3OH at 110 K. All of the ion intensities are determined from peak heights and are reported relative to the intensity of the CH_3OHH^+ ion at 110 K.

Although the evaluation of the intensity of the CH_3^+ signal is complex, we believe there are only two significant origins of this species and its behavior may be well understood. The largest source is from the ion-beam-induced cracking of the CH_3OH molecule itself. As we have already shown, the CH_3^+ ion yield from multilayer CH_3OH is quite high. It is also possible that CH_3^+ ions could arise from the ion-beam-induced fragmentation of OCH_{3ads}. As noted above, studies on Pd{111} predosed with oxygen are known to produce a pure OCH_{3ads} overlayer.[6] The analysis of the SIMS spectra as a function of surface temperature for this overlayer suggests that no significant CH_3^+ ion signal results from the formation of OCH_{3ads}.[33] Further, a SIMS investigation of CH_3OD thermal decomposition on O/P{111}[34] conclusively demonstrates that the CH_3^+ ion yield from OCH_{3ads} is negligible when compared to that from CH_3OH_{ads}. Presumably, the electronegative O atom enhances the formation of negative ions while inhibiting the formation of positive ions. A last, but important, possible source of CH_3^+ is from an adsorbed CH_3 species. This SIMS cluster ion has been observed previously from Ni surfaces exposed to high pressures of CO and H_2.[35] The CH_3^+ signals might arise from recombination during desorption of $=CH_2$ or $\equiv CH$ surface species with H^+. For this process to be possible, however, the CH_2^+ and CH^+ ion signals must also be present to satisfy this scenario.[35] For the case of Pd{111} under the experimental conditions described here we observe no significant intensity from these species. Thus, the CH_3^+ ion signal arises mainly from CH_3OH cracking at temperatures below the CH_3OH desorption temperature but arises mainly from CH_{3ads} above this temperature.

In our experiment, the intensity of the CH_3^+ ion decreases substantially as the temperature is raised from 110 to 200 K, indicating desorption of CH_3OH_{ads}. Above 200 K no CH_3OH_{ads} remains to produce a CH_3^+ ion signal. Since, as already noted, significant CH_3^+ ion intensity from OCH_{3ads} is not detected,[33,34] we believe the signal above 175 K arises from trace CH_{3ads}. This signal correlates with the low-binding-energy C 1s peak seen at 175 and 275 K.

A significant increase in the H_2O^+ SIMS ion signal is observed between 110 and 175 K. The origin of this signal is not certain at this stage. It may arise from an unavoidable H_2O impurity in the CH_3OH sample. As reported in the next section, the relative intensity of this species is considerably lower when using lower initial CH_3OH exposures. It may also arise from a high local concentration of CH_3OH which may contribute to matrix ionization effects. Above 175 K the H_2O^+ intensity rapidly decreases to nearly zero at 225 K and is not detected at 250 K. Because no H_2O is observed in the TPD of CH_3OH on Pd{111},[16] we

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Table I. Summary of CH_3OH Reactivity of Pd{111}

	initial exposure langmuirs		
temp, K	1–1.5	2	6
110	CH_3OH_{ads}	CH_3OH_{ads} + partial multilayer	CH_3OH_{ads} + several multilayers
125–225	$CH_{3ads} + H_2O_{ads} + OCH_{3ads}$	$CH_{3ads} + H_2O_{ads} + OCH_{3ads}$, multilayer desorbs	$OCH_{3ads} + H_2O_{ads}$ + trace CH_{3ads}, multilayer desorbs
225–275	$CH_{3ads} + OCH_{ads}{}^{a} + H_{ads} + O_{ads}$	$CH_{3ads} + OCH_{3ads}{}^{a} + H_{ads} + O_{ads}$	*b*
275–350	$O_{ads} + CH_x$ ($x \leq 3$), H_2 desorbs	$O_{ads} + CH_x$ ($x \leq 3$), H_2 desorbs	*b*
350–490	$O_{ads} + C_{ads}$	$O_{ads} + C_{ads}$	*b*
>490	CO desorbs	CO desorbs	CO desorbs

[a] We cannot be sure of the precise nature of this product in this temperature range although evidence points to an assignment of this species to an oxyhydrocarbon. See text for further information. [b] Not examined in this work.

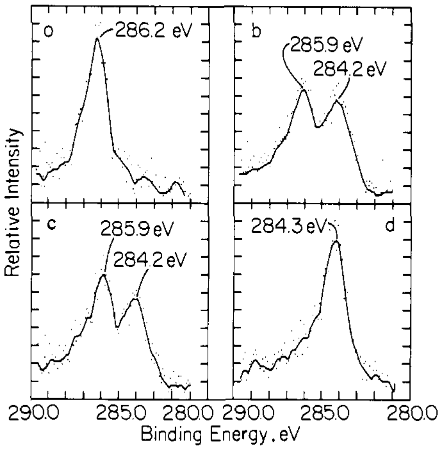

Figure 10. Carbon 1s XPS spectra for Pd{111} exposed to 1.5 langmuirs of CH_3OH at (a) 110 K, (b) heated to 225, (c) heated to 300 K, and (d) heated to 400 K.

attribute this decrease to *decomposition* to H_{ads} and O_{ads} rather than to H_2O desorption. As further evidence for this decomposition pathway we note that there is a stoichiometric decrease of the C 1s intensity above 400 K, presumably due to CO desorption, which could not occur if H_2O desorbed above 250 K. This information is summarized in Table I.

CH_3OH Exposures of 1–2 Langmuirs. The reaction pathway for CH_3OH adsorbed on Pd{111} at 110 K after exposures between 1 and 2 Langmuirs is clearly dominated by decomposition rather than desorption. The important data to support this thesis are presented in Figure 10, where the XPS spectra are reported for various temperatures after 1.5-langmuir CH_3OH exposure and in Figures 11 and 12 where the temperature dependence of the important SIMS ions is seen after 1- and 2-langmuir CH_3OH exposures. By comparing our XPS and SIMS results, by utilizing related TPD and EELS experiments from other laboratories, and by incorporating spectral assignments deduced from the 6-langmuir exposure case, we feel that it is possible to extract rather detailed insight into the decomposition mechanism.

At 110 K, 1.5-langmuir exposure of CH_3OH produces one monolayer of CH_3OH_{ads}. This conclusion is clear from the data presented in Figure 6 and from the single C 1s peak at 286.2 eV seen in Figure 10a. The presence of intense CH_3OHH^+, CH_2OH^+, and $CH_3{}^+$ ions seen for the 1- and 2-langmuir exposures in Figures 11 and 12 also suggests that only molecular CH_3OH is present on the surface.

Upon heating to 225 K, the story immediately begins to get quite complicated. As shown in Figure 10b, the single C 1s XPS peak splits into a doublet while keeping approximately the same total area. Moreover, the CH_3OH-related SIMS ions, except for $CH_3{}^+$ (and H_2O^+), are no longer detectable as seen in both Figures 11 and 12. This picture remains nearly unchanged as the crystal is heated through 300 to nearly 400 K where the SIMS signals nearly disappear and a single XPS peak reemerges albeit at a different E_b value of 284.3 eV.[36]

Let us first consider the doublet seen in the XPS spectrum of Figure 10b,c. There are several pieces of data that move us to assign the 285.9-eV peak to OCH_{3ads} and the 284.2-eV peak to CH_{3ads}. Pertaining to the methoxide adsorbate, we have already noted that the C 1s E_b value of OCH_{3ads} is precisely 285.9 eV. It is conceivable, however, that this peak is associated with CO_{ads}. As seen in Figure 13, the C 1s E_b value for Pd{111} exposed to 10 langmuirs of CO at 300 K is observed to occur at virtually the same energy and with the same intensity as that seen for CH_3OH adsorbed at 100 K and heated to 225 K. We feel that it is possible to rule out the presence of CO_{ads} in our situation for two very compelling reasons. First, the O_{KLL} Auger spectra shown in Figure 14 are clearly different for adsorbed CO and adsorbed CH_3OH. Note that the kinetic energy of the CH_3OH feature is nearly 2 eV higher than that of the CO feature and that its intensity is considerably reduced. This reduction in intensity presumably arises from the opposite surface orientation of –CO versus –OCH_3 and from the additional shielding produced by the hydrogen atoms. A second piece of data that is important in ruling out the presence of CO is that no significant $PdCO^+$ ion signal is observed by SIMS at temperatures up to 400 K. This molecular cluster is typically

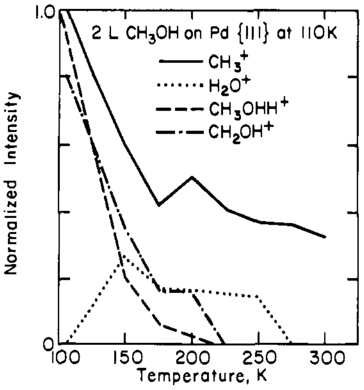

Figure 11. Intensity of selected positive secondary ions versus surface temperature for Pd{111} exposed to 2 langmuirs of CH_3OH initially at 110 K. The ion intensities are determined from peak heights and are reported relative to the CH_3OHH^+ ion signal at 110 K. The spectra were recorded by using a 3-keV Ar^+ primary ion beam with a current density of 2 nA·cm^{-2}.

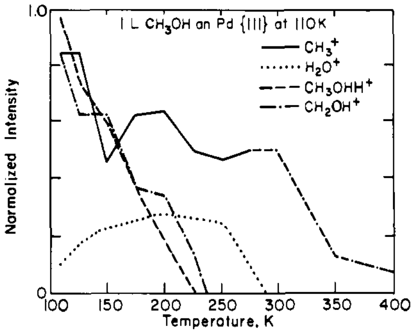

Figure 12. Intensity of selected positive secondary ions versus surface temperature for Pd{111} exposed to 1 langmuir of CH_3OH initially at 110 K. The ion intensities are determined from peak heights and are reported relative to the CH_3OHH^+ ion signal at 110 K. The spectra were recorded by using a 3-keV Ar^+ primary ion beam with a current density of 0.4 nA·cm^{-2}.

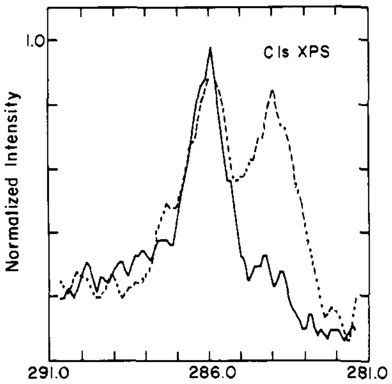

Figure 13. Carbon 1s XPS spectra for Pd{111} exposed to 10 langmuirs of CO at 300 K (—) and Pd{111} exposed to 3 langmuirs of CH_3OH at 110 K and heated to 225 K (---). The relevant peak maxima occur at 286.1 eV for CO and at 285.9 eV for CH_3OH. Similar intensity scales were employed for each spectra.

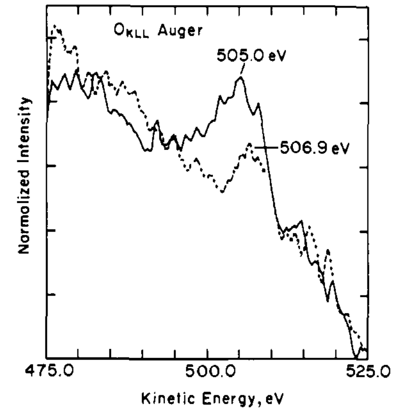

Figure 14. Oxygen KLL Auger spectra for Pd{111} exposed to 10 langmuirs of CO at 300 K (—) and Pd{111} exposed to 3 langmuirs of CH_3OH at 110 K and heated to 225 K (---). The kinetic energies associated with the peak maxima are indicated in the figure. The relation of intensities between the two spectra are the same ones that were used in Figure 13.

very stable and is a sensitive indicator of the presence of CO.

It is also conceivable that the 285.9-eV peak observed at 225 K is somehow associated with CH_3OH_{ads}. This possibility is not likely since the TDS spectrum for CH_3OH adsorbed on Pd{111} shows that multilayer desorption occurs at 147 K and that the remaining chemisorbed molecules desorb at 180 K. Further, the molecular desorption feature on Pd{111} has been shown to occur by at least 200 K for adsorption at 170 K. Finally, the possibility that CH_3OH_{ads} is associated with the 285.9-eV peak may be ruled out since, as seen in Figure 11, the CH_3OHH^+ and CH_2OH^+ ion signals attributable to CH_3OH have disappeared by 225 K.

We conclude that the 285.9-eV C 1s feature at 225 K is an oxyhydrocarbon species other than CH_3OH_{ads} and is most probably OCH_{3ads}. The presence of an alternative oxyhydrocarbon is supported by the TDS spectra of CH_3OH adsorbed on Pd{111} at 170 K. These measurements show that there is a CO and H_2 peak well above the CH_3OH molecular desorption temperature. These results suggest that an oxyhydrocarbon species is present in addition to CH_3OH_{ads} until at least 300 K. Moreover it has been shown that OCH_{3ads} may form on Pd{100} at temperatures as low as 80 K and remain on the surface to temperatures up to at least 300 K. On Pd{111}, however, it has been suggested that the η^2-(C–O)[16] formaldehyde species forms upon further heating to 300 K. From our measurements we could not definitely confirm this assignment. Experiments on the O-precovered Pd{111} surface,[33] however, do suggest the formation of a formaldehyde adsorbate at approximately 175 K.

The presence of the peak at 284.2 eV is particularly striking, and identification of the intermediate associated with this feature is clearly important. In a generic sense, hydrocarbon fragments that do not contain electronegative heteroatoms like oxygen are typically observed near 284 eV. The ability of XPS to identify specific types of these molecular fragments is not high. Fortunately, however, interpretation of the SIMS data is very clear between 225 and 300 K. Since OCH_{3ads} does not produce significant intensities of positive ions and since no molecular CH_3OH remains on the surface at 225 K, the carbon-containing SIMS ions in this temperature range must correspond with the 284.2-eV XPS species. The only observable SIMS ion with these characteristics is CH_3^+. Since the SIMS result is conspicuously missing contributions of C^+, CH^+, and CH_2^+ ions, we believe the only possible assignment of the 284.2-eV peak is to CH_{3ads}. Thus, between 225 and 300 K the data show that OCH_{3ads} and CH_{3ads} are the only carbon-containing fragments on the surface and that these species are present in approximately equal concentrations.

At 400 K, only one C 1s peak is observed at 284.3 eV. This carbon species is presumably hydrogen deficient since most of the surface hydrogen is observed to have desorbed by this temperature.[16] The small shift from 284.2 eV seen in Figure 10c to 284.3 eV shown in Figure 10d is also consistent with this notion.[36] At 600 K only trace carbon remains on the surface at an E_b value of 284.6 eV. This observation suggests that virtually all of the C_{ads} has combined with O_{ads} to desorb as CO at 490 K. The E_b value suggests that the remaining carbon is present as amorphous carbon.[37]

We note that evidence for the ability of Pd surfaces to activate the methanolic C–O bond has been indirectly implied previously. In one instance,[38] a CH_4 feature was detected in the TDS spectrum for CH_3OH adsorbed at 220 K on Pd{111}. In a second instance,[39] CH_4 as well as C_2H_6 were observed to desorb from a thin Pd film exposed to CH_3OH at 223 K.

There are a number of points that arise when examining Figures 10–12 that require further elaboration. For 1-langmuir exposure shown in Figure 12 the coverage is well below the saturation point and all of the CH_3OH that adsorbs undergoes decomposition. In the subsaturation exposure regime the CH_3^+ intensity as a function of temperature should be controlled by two surface reactions. The first is the decomposition of CH_3OH_{ads} to OCH_{3ads}. This pathway accounts for the decrease in the CH_3^+ intensity seen between 110 and 150 K and has been previously observed for CH_3OD decomposition on O/Pt{111}.[34] The second is the decomposition of CH_3OH_{ads} to CH_{3ads} and OH_{ads}. This pathway may account for the increase in H_2O^+ intensity above 110 K and for the increase in the CH_3^+ intensity above 150 K. If, as we propose, activation of the methanolic CO bond is necessary for the formation of the H_2O^+ signal, CH_{3ads} and OCH_{3ads} must form simultaneously at temperatures as low as 125 K since the C–O bond cleavage provides an oxygen site that is known to enhance the formation of OCH_{3ads}.[4,6,7,13–15] Note that the temperature at which the CH_3^+ ion intensity begins to increase is 25 K lower after 1-langmuir exposure than after 2-langmuir exposure. This difference probably reflects the fact that CH_3OH_{ads} contributes substantially to the CH_3^+ SIMS yield for the 2-langmuir exposure case. Thus, below 200 K for subsaturation exposures the reaction sequence may be summarized as follows:

$$2CH_3OH_{ads} \rightarrow CH_{3ads} + OCH_{3ads} + H_2O_{ads}$$

With this mechanism, one molecule of CH_{3ads} is produced for each molecule of OCH_{3ads}, in accord with Figure 10b,c. Also apparent from Figure 10 is the fact that virtually all of the CH_3OH adsorbed at 1.5 langmuirs (saturation coverage) decomposes to CH_3OH_{ads} and CH_{3ads}. By comparison to the C 1s intensity for saturation CO adsorption shown in Figure 13, we estimate that

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(36) In our earlier paper, we reported this number to be 284.2 eV. Additional experiments and data analysis, however, have convinced us that the small shift to 284.3 eV in Figure 10d is, in fact, occurring.

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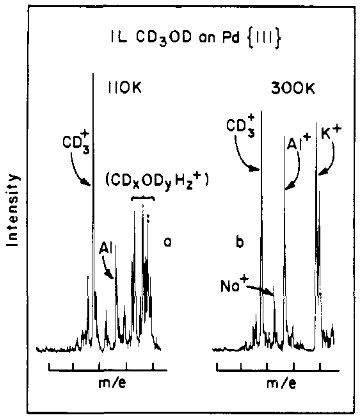

Figure 15. Positive ion SIMS spectra of Pd{111} exposed to 1 langmuir of CD_3OD. In these experiments the spectra were recorded at 110 K (a) and then the sample was rapidly heated to 300 K with the incident ion beam turned off (b). The incident ion beam current was 0.4 nA·cm^{-2} and was incident on the sample for a total time of less than 500 s for a total dose of less than 1.5 × 10^{12} ions·cm^{-2}.

the coverage of the sum of the CH_3O_{ads} and the CH_{3ads} is between one-quarter and one-half monolayer.

The CH_3^+ ion intensity reaches a maximum at 200 K and is relatively stable as the temperature is raised to 325 K. The decrease in the CH_3^+ ion intensity between 200 and 300 K may be due in part to a change in ionization probability arising from the decomposition of H_2O_{ads} to H_{ads} and O_{ads} at 225 K. A second factor in this decline is that approximately 15% of the total surface species is removed by the cumulative primary ion dose delivered to the crystal by the time the temperature reaches 300 K. Although this perturbation is annoying, we have shown that it does not alter the interpretation of our results by performing an experiment where the crystal is immediately heated from 110 to 300 K and then analyzed by SIMS with a much smaller ion dose. The results are shown in Figure 15. In this experiment only 5% of the CD_3^+ signal is lost upon heating to 300 K.

An interesting small point in the comparison of Figures 11 and 12 is that between approximately 175 and 225 K, the CH_2OH^+ ion is slightly more intense than the CH_3OHH^+ ion. Similar results are obtained for CH_3OH decomposition on O/Pt{111}.[34] On both surfaces, there is an increase in the *m/e* 31 ion intensity when an increase in the CH_3^+ ion intensity is detected. We attribute this effect to an ion-beam-induced combination of CH_{3ads} with OH_{ads} or H_2O_{ads} during the particle ejection event. This idea is supported by analysis of the 6-langmuir desorption/decomposition plot shown in Figure 9, where only trace CH_{3ads} is formed. Note that for this case no significant increase in the CH_2OH^+ ion is observed when compared to the CH_3OHH^+ ion at temperatures between 175 and 225 K.

The plot of the CH_3^+ ion intensity above 275 K, the dotted line in Figure 12, suggests that the CH_{3ads} begins to decompose at 350 K. By 400 K, the high-current SIMS spectra, not shown, reveals that trace C, CH, and CH_2 species have increased an order of magnitude in relation to the CH_3^+ ion, but the CH_3 signal is still the most intense. The fact that CH_3^+ is the only ion observed at 300 K and is the most intense ion detected at 400 K suggests an unusual stability of CH_{3ads} on Pd{111}. A summary of all the important surface chemical information is provided in Table I.

Coverage-Dependent Reactivity. The SIMS and XPS experiments suggest that at near saturation coverages, the decomposition reaction of CH_3OH to OCH_{3ads}, CH_{3ads}, and H_2O_{ads} competes quite well with the simple CH_3OH desorption channel. Upon increasing the CH_3OH exposure, the formation of CH_{3ads} is reduced to trace levels. This type of coverage-dependent reactivity is unusual but not unprecedented. On Cu{110} site blocking, by an adsorbed CH_3OH_{ads} multilayer formed at 140 K, reduced the amount of OCH_{3ads} that was produced by a factor of 2 when compared to the case where CH_3OH was initially adsorbed at 270 K.[30] Site blocking has also been invoked to explain the decrease in OCH_{3ads} formation on O-predosed Cu{110},[30] Cu{111},[9] and Ru{001}[13] surfaces. The decrease in CH_{3ads} formation for 6 langmuirs of CH_3OH on Pd{111} may also arise from a site-blocking mechanism since a multilayer is present under these conditions. Another factor, however, is that the SIMS measurements suggest that H_2O forms on the surface at high CH_3OH exposures as seen in Figure 9. As previously noted, the H_2O_{ads} may form from a surface reaction or may be present as a trace impurity in CH_3OH. In either case, the presence of these oxygen-containing surface species appears to be extremely effective in blocking the CH_{3ads} reaction channel. Finally, we note that the reduction in hydrocarbon overlayer stability with high CH_3OH exposure is consistent with previous EELS measurements.[6] In this case, no evidence for any hydrocarbon species was observed at 300 K after adsorption of 30 L CH_3OH on Pd{111} at 140 K.

Conclusions

In this paper we have provided experimental evidence for a new decomposition pathway for CH_3OH on Pd{111} that involves direct activation of the C–O bond and the formation of a stable $-CH_{3ads}$ surface intermediate. Although we find that this reaction occurs only when the Pd{111} surface is atomically clean *and* only after subsaturation initial exposures of CH_3OH, we feel that the results are significant for several reasons:

There have been few studies where stable $-CH_3$ intermediates have been found on metal surfaces.[35,40,41] Whether this is due to paucity of situations where $-CH_3$ is formed or whether conventional surface science techniques have heretofore been insensitive to the presence of $-CH_3$ is not yet clear. In either event, it will now be of interest to examine the detailed formation and decomposition mechanisms associated with this most basic hydrocarbon surface intermediate by using many other organic precursors. As a first example of this effort, it now appears that $-CH_3$ is also formed on both clean and oxygen-predosed Pt{111} surfaces.[34]

Although it is always dangerous to relate mechanistic observations from UHV single-crystal surface science studies to the mechanism of heterogeneous catalytic reactions, there are a few obvious implications of our work that merit consideration in this regard. If CH_3 is an important surface intermediate, it would be available to combine with other surface species such as H, O, OH, and other CH_3 molecules to produce CH_4, CH_3OH, CH_3OCH_3, and CH_3CH_3. It is interesting that all of these products are observed to form on both pure and supported Pd catalysts from CO and H_2 reactants. As a corollary to this thesis, we have also reported that CH_3 decomposes near 220 K on Pt rather than near 400 K as on Pd.[42] Platinum catalysts produce CH_3OH, but with an order of magnitude lower rate than that observed on Pd.

Our results indicate that under appropriate conditions, the metal surface may activate both the C–O and O–H bonds of CH_3OH. Although not previously reported, this observation is certainly not surprising in view of the fact that both of these bond energies are quite similar. The C–O bond energy is 3.9 eV, and the O–H bond energy is 4.5 eV.

And finally, we believe that we have demonstrated that the combination of XPS and SIMS is a powerful and unique approach for studying this type of reaction. In this case, XPS provides quantitative elemental surface composition data along with general guidelines regarding the types of molecular fragments that may be present. The SIMS cluster ions, on the other hand, yield powerful structural data about these molecular fragments.

Acknowledgment. We are grateful to the National Science Foundation, the Office of Naval Research, and the IBM Corp. for partial support of this work. We also appreciate a number of stimulating discussions with Greg Geoffroy, Al Vannice, and Jr.-Jyan Chen that have contributed to the crystallization of the ideas presented herein.

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