

Methanolic C–O Bond Activation on Pd{111}: A Coverage-Dependent Reaction

Jr-Jyan Chen and Nicholas Winograd*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Received August 16, 1991

We find that the previously reported methanolic C–O bond activation on Pd{111} to form adsorbed methyl and hydroxyl at 225 K¹ occurs only for initial methanol coverages near 1 monolayer. At lower and higher coverages, methanol decomposes via the more traditional methoxy intermediate. Moreover, when methyl is formed, it is not observed to decompose until the temperature is raised to 400 K. This thermal behavior is quite unusual since CH₃ has been observed to combine with H to desorb as CH₄ below 300 K,^{2–5} dimerize to produce C₂H₆ below 200 K,^{6,7} or dehydrogenate to form CH₂ and H below 200 K.⁸ In addition, we find that methyl undergoes sequential dehydrogenation as the temperature is increased to form CH₂ at 400 K, CH at 500 K, and C at >500 K. We speculate that the coverage dependency is connected with the thermal stability of CH₃ by a site-blocking mechanism, probably involving CO.

Although methylidyne, methylene, and methyl have been proposed to be the fundamental building units in catalytic methanation and Fischer–Tropsch synthesis,^{9,10} direct evidence of such radicals on a well-defined single crystal under ultrahigh vacuum conditions is sparse.^{1,8,11–13} Using X-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS), we previously reported direct evidence for CH₃ and OCH₃ formation on Pd{111} during CH₃OH decomposition after initial exposures of ~1.25 L (1 L = 10⁻⁶ Torr s),¹ where 1 monolayer corresponds to ~1.3-L exposure. These conclusions were questioned in subsequent work from data produced by a series of isotope scrambling experiments which showed that the CO bond remained intact during methanol decomposition.¹⁴ Many other confusing reports concerning the reactivity of simple hydrocarbons abound in the literature,^{15–18} and it is important to establish the experimental parameters which allow the critical mechanistic pathways to emerge.

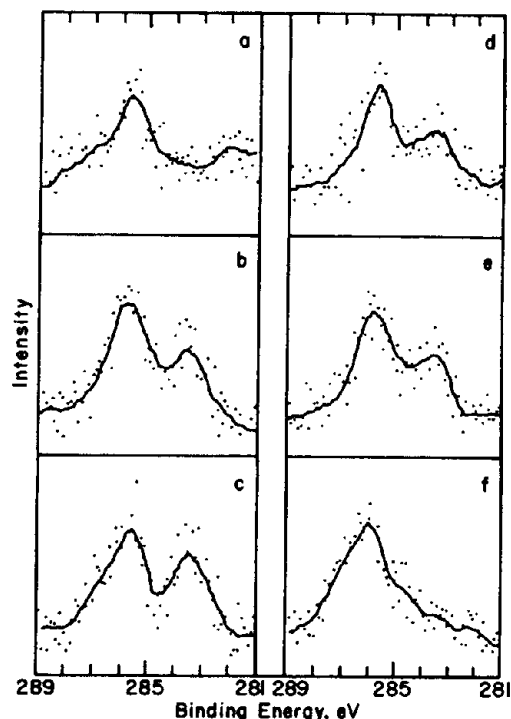


Figure 1. Carbon 1s XPS spectra for Pd{111} exposed to (a) 0.75 L, (b) 1.00 L, (c) 1.25 L, (d) 1.50 L, (e) 1.75 L, and (f) 2.00 L of methanol at 105 K and then heated to 300 K. The spectra are reported without normalization.

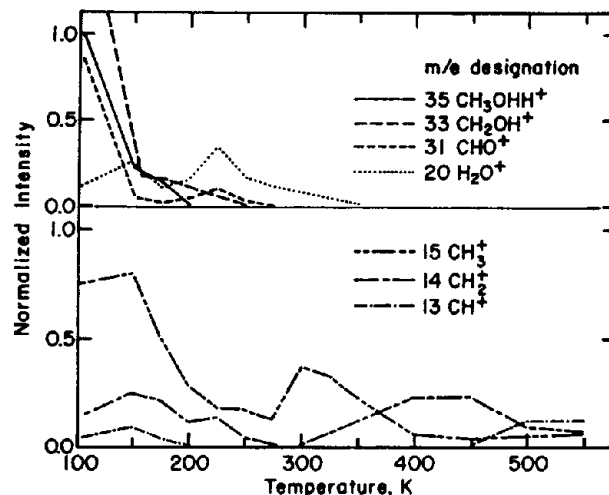


Figure 2. Intensity of selected positive secondary ions versus surface temperature for Pd{111} exposed to 1.25 L of CH₃¹⁸OH initially at 105 K. The ion intensities are determined from peak heights and reported relative to the CH₃¹⁸OHH⁺ ion signal at 105 K. Spectra were recorded with an Ar⁺ ion beam energy of 3.0 KeV and an ion beam current density of 2 nA/cm².

- (1) Levis, R. J.; Jiang, Z.; Winograd, N. *J. Am. Chem. Soc.* **1988**, *110*, 4431; **1989**, *111*, 4605.
- (2) Steinbach, F.; Kiss, J.; Krall, R. *Surf. Sci.* **1985**, *157*, 401.
- (3) Zhou, X. L.; Yoon, C.; White, J. M. *Surf. Sci.* **1988**, *206*, 379.
- (4) Benziger, J. B.; Madix, R. J. *J. Catal.* **1980**, *65*, 49.
- (5) Henderson, M. A.; Mitchell, G. E.; White, J. M. *Surf. Sci.* **1987**, *184*, L325.
- (6) Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1986**, *108*, 2881.
- (7) Zhou, X. L.; Solymosi, F.; Blass, P. M.; Cannon, K. C.; White, J. M. *Surf. Sci.* **1989**, *219*, 294.
- (8) Lee, M. B.; Yang, Q. Y.; Tang, S. L.; Ceyer, S. I. *J. Chem. Phys.* **1986**, *85*, 1693.
- (9) Bell, A. T. *Catal. Rev.—Sci. Eng.* **1981**, *23* (1, 2), 203.
- (10) Lee, G. v. d. *Catal. Rev.—Sci. Eng.* **1987**, *29* (2, 3), 183.
- (11) Kaminsky, M. P.; Winograd, N.; Geoffroy, G. L.; Vannice, M. A. *J. Am. Chem. Soc.* **1986**, *108*, 1315.
- (12) George, M. P.; Avery, N. R.; Weinberg, W. H.; Tebbe, F. N. *J. Am. Chem. Soc.* **1983**, *105*, 1393.
- (13) Demuth, J. E.; Ibach, H. *Surf. Sci.* **1978**, *78*, L238.
- (14) Guo, X.; Yates, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 3155.
- (15) Kruse, N.; Rebholz, M.; Matolin, V.; Chuah, G. K.; Block, J. H. *Surf. Sci.* **1990**, *238*, L457.
- (16) Wang, J.; Masel, R. I. *J. Am. Chem. Soc.* **1991**, *113*, 5850.

Experiments were conducted in a multitechnique surface analysis system described previously.¹⁹ The procedures for cleaning a Pd{111} crystal and purifying methanol and the spectroscopic protocols involving binding-energy referencing, peak deconvolution, and static SIMS measurements have been described in detail.¹ Methanol exposures are corrected by an ion gauge sensitivity factor of 1.9.²⁰ All spectra were recorded after the sample was warmed to the desired temperature at ~1 K/s and recooled to near the adsorption temperature of 105 K.

- (17) Rebholz, M.; Kruse, N. *J. Chem. Phys.* **1991**, *95*, 7745.
- (18) Solymosi, F.; Révész, K. Submitted to *J. Am. Chem. Soc.*
- (19) DeLouise, L.; Winograd, N. *Surf. Sci.* **1984**, *138*, 417.
- (20) Summers, R. L. NASA Technical Note TND-5285; **1969**.

Figure 1 shows the C 1s photoelectron spectra for a clean Pd{111} sample exposed to a series of different methanol exposures at 105 K and subsequently heated to 300 K. The peaks with BEs of 285.8 and 283.8 eV are assigned to OCH₃ and CH₃, respectively.¹ The formation of CH₃ exhibits a striking dependence on the initial coverage of methanol, forming only between exposures of 1.00 and 1.75 L. This requirement suggests that there is a specific arrangement of methanol molecules occurring near monolayer coverage on the Pd surface which is required to activate the C-O bond, perhaps involving hydrogen bonding between OH units of adjacent methanol molecules.²¹ Although the details of the initial coverage effect is still an open question, the observation would certainly explain the variability of results obtained with this seemingly straightforward model system.

The temperature dependence of CH₃ formed by a 1.25-L exposure of methanol to Pd{111} at 105 K is striking. The methanol itself remains molecularly adsorbed until the temperature is increased to 225 K. At this point, the single C 1s peak at 286.2 eV splits into two peaks at 285.8 and 283.8 eV as noted above. Thereafter, the surface OCH₃ and CH₃ species undergo two independent reaction channels. The high binding energy peak shifts slightly, to 286.0 eV, by 400 K, suggesting decomposition of OCH₃ to CO and H₂. Above 400 K, CO and H₂ desorption is observed, accompanied by a gradual shift of the 283.8-eV peak toward 285.0 eV. This trend suggests that the CH₃ species is undergoing a decomposition reaction, presumably involving dehydrogenation, where the products are characterized by using SIMS as discussed below.

The positive-ion SIMS peak intensities as a function of temperature after exposing Pd{111} 1.25 L of CH₃¹⁸OH at 105 K are shown in Figure 2. The intensities of methanol ions (*m/e* = 35, 33, 31) and CH_x⁺ ions decline concurrently as the temperature is increased from 105 to 275 K. This result indicates that in this temperature range molecularly adsorbed methanol either desorbs or decomposes into other species. When the surface temperature reaches 300 K, however, the CH₃⁺ ion intensity increases and

CH₃⁺ is the major carbon-containing secondary ion. This ion correlates with the XPS C 1s peak at 283.8 eV seen in Figure 1 and is associated with CH₃. Note the development of secondary ions with *m/e* 14 and 13 at 400 and 500 K, respectively, which eventually ends up with a mixed phase of CH_x (*x* = 0-3) at 550 K. The appearance of CH_x (*x* < 3) secondary ions is consistent with the XPS C 1s peak shift from 283.8 to 285.0 eV and indicates that a stepwise dehydrogenation of CH₃ occurs at *T* ≥ 400 K. This unusual stability of CH₃ on the Pd{111} is generally not found on clean metal surfaces above 300 K. In our case, however, the CH₃ species is stable to the temperature where CO begins to desorb from the surface. Hence, it is possible that CO chemisorption may block the dehydrogenation or recombination of CH₃. A similar site-blocking mechanism has been observed for C₂ fragments coadsorbed with CO on Ni{001} and Ru{001}.²²

We believe that the results presented here are important for several reasons. (1) The formation of CH₃ from CH₃OH is found to occur over a very limited initial coverage of methanol. This observation implies that the formation of CH₃ is contingent upon a special molecular arrangement of precursors before reaction and that the CH₃ product is stabilized by ancillary reaction products, such as CO. (2) The dramatic dependence of the reaction pathway on initial reaction conditions helps to explain divergent observations from other laboratories. (3) The combination of XPS and SIMS provides a unique approach for examining the fate of these important reaction intermediates.

Acknowledgment. We appreciate many helpful discussions with Dr. Ying Zhou and Dr. Robert J. Levis. Financial support from the National Science Foundation, the Office of Naval Research, and the Department of Energy is gratefully acknowledged.

Registry No. Methanol, 67-56-1; palladium, 7440-05-3.

(21) Peremans, A.; Maseri, F.; Darville, J.; Gilles, J.-M. *Surf. Sci.* **1990**, *227*, 73.

(22) Akhter, S.; Henderson, M. A.; Mitchell, G. E.; White, J. M. *Langmuir* **1988**, *4*, 246.