

Evidence for Activation of the C-O Bond of Methanol on the Pd{111} Surface after Low-Temperature Adsorption

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Direct evidence, using secondary ion mass spectroscopy (SIMS) supported by X-ray photoelectron spectroscopy (XPS), has been obtained for the activation of the C-O bond of methanol after adsorption at 110 K on the Pd{111} surface. In our experiments we find that the C-O bond dissociates after heating to 175 K leaving CH_3ads (methyl) and $\text{H}_2\text{O}_{\text{ads}}$, as evidenced by prominent SIMS signals at m/e 15 and 18, respectively. Methoxide ($\text{CH}_3\text{O}_{\text{ads}}$) is produced simultaneously and has been identified by its carbon 1s photoelectron binding energy. In addition to reporting the first observation of methanolic C-O bond activation on a well-defined transition-metal surface¹ we also report the discovery of a stable methyl species on Pd{111} as the surface is heated from 175 to 400 K. This observation has mechanistic implications for the uniquely selective formation of methanol from CO and H_2 on Pd catalysts.² Previously, only $\text{CH}_3\text{O}_{\text{ads}}$ has been found on

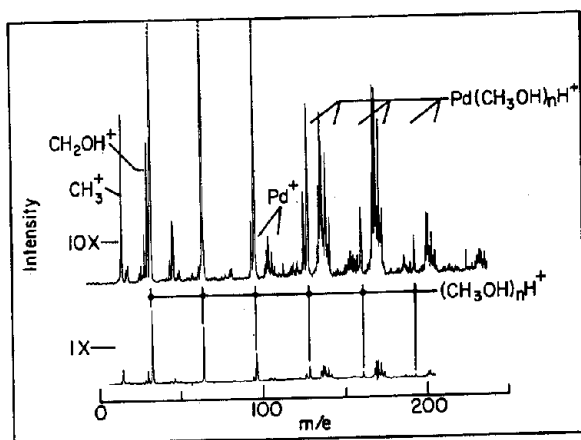


Figure 1. The SIMS spectrum for a 5 L methanol exposure to Pd{111} at 110 K. The primary ion current is 0.4 nA/cm².

(1) Steinbach, F.; Krall, R.; Cai, J. X.; Kiss, J. In *Proceedings of the 8th International Congress on Catalysis*; Berlin, July 1984; Vol. 3 (Verlag Chemie: Weinham, 1984) p III-359. The dissociation of the CO bond of methanol on a Ni foil under a high flux of methanol molecules (1×10^{16} $\text{CH}_3\text{OH cm}^{-2} \text{ s}^{-1}$) at 190 K is reported. A subsequent study by Russell et al. (Russell, J. N.; Chorkendorff, I.; Yates, J. T. *Surf. Sci.* 1987, 183, 316) proved that under similar conditions, the Ni{111} surface does not dissociate the CO bond of methanol.

(2) Poutsma, M. L.; Elek, L. F.; Ibarbia, P. A.; Risch, A. P.; Rabo, J. A. *J. Catal.* 1978, 52, 157.

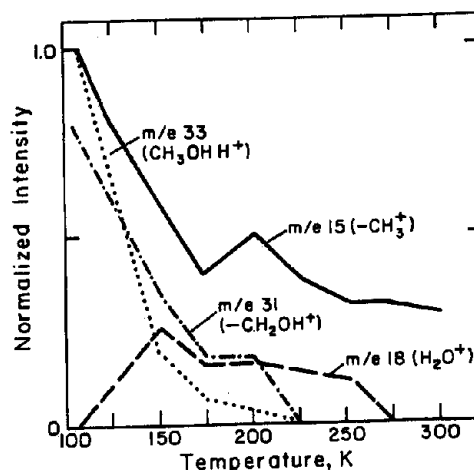


Figure 2. Secondary ion intensity versus surface temperature for a 2 L methanol exposure to Pd{111} initially at 110 K. The primary ion current is 0.4 nA/cm².

single-crystal transition-metal surfaces³⁻⁶ exposed to CH_3OH at low temperatures and subsequently heated between 140 and 200 K. Additionally, the formation of $\text{CH}_3\text{O}_{\text{ads}}$ at low temperatures was found to be enhanced by preposing the transition-metal surface with O_2 at 300 K.⁷⁻⁹

The apparatus used for these experiments has been described in detail previously.¹⁰ The Pd{111} surface was rigorously cleaned by cycles of argon ion sputtering ($2 \mu\text{A cm}^{-2}$) for 5 min followed by annealing to 1200 K prior to each experiment. After this treatment the surface then proved to be free of impurities as determined by SIMS and XPS. The methanol was distilled and subjected to several freeze-pump-thaw cycles before use. The exposures listed throughout this letter are in units of Langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr-s}$) and are reported as corrected ion gauge readings.

The SIMS spectrum for 5 L CH_3OH on Pd{111} at 110 K is shown in Figure 1. The prominent peaks, marked in the figure, are assigned to CH_3^+ at m/e 15, CH_2OH^+ at m/e 31,¹¹ and CH_3OHH^+ at m/e 33 as well as to additional hydrogenated n-mers observed at higher mass. In Figure 2, the intensities of

(3) Christmann, K.; Demuth, J. E. *J. Chem. Phys.* 1982, 76, 6308.

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(5) Demuth, J. E.; Ibach, H. *Chem. Phys. Lett.* 1979, 60, 395.

(6) Waddill, G. D.; Kesmodel, L. L. *Surf. Sci.* 1987, 182, L248.

(7) Felner, T. E.; Weinberg, W. H.; Lastushkina, G. Y.; Zhdan, P. A.; Borek, G. K.; Hrbek, J. *Appl. Surf. Sci.* 1983, 16, 351.

(8) Gates, J. A.; Kesmodel, L. L. *J. Catal.* 1983, 83, 437.

(9) Wachs, I. E.; Madix, R. J. *J. Catal.* 1978, 53, 208.

(10) DeLouise, L. A.; Winograd, N. *Surf. Sci.* 1984, 138, 417.

(11) A similar experiment using CD_3OH revealed an ion at m/e 33 rather than an ion at m/e 34 implying the presence of CD_2OH^+ rather than CD_3O^+ .

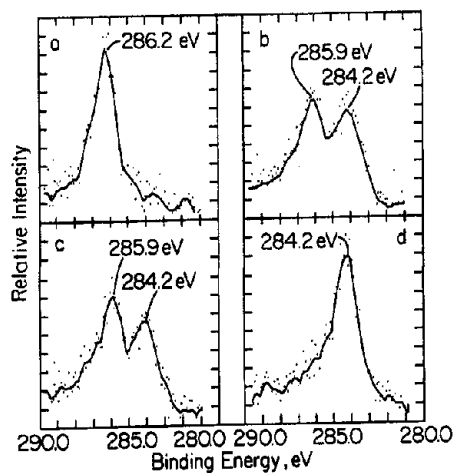


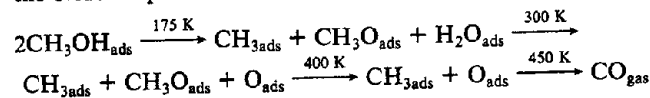
Figure 3. Carbon 1s XPS spectra for a 1.5 L exposure of methanol to Pd{111}: (a) 110 K; (b) heated to 225 K; (c) heated to 300 K; (d) heated to 400 K.

several ions resulting from a 2 L CH₃OH exposure are shown as the surface is heated from 110 K. This picture reveals that the intensity of the methanol-related secondary ions, CH₂OH⁺ and CH₃OHH⁺, decrease to zero at 225 K, while the CH₃⁺ and the H₂O⁺ ions signals increase and then eventually decrease at higher temperatures. These trends, along with the corresponding XPS C 1s intensity measurements for a 2 L exposure,¹⁴ suggest that as the surface is heated, approximately 1/4 of the CH₃OH desorbs from the surface while the remaining 3/4 of the CH₃OH dissociates at the C-O or O-H bond. By 300 K the only SIMS signal apparent is at *m/e* 15. Since the CH₃⁺ ion yield from CH₃O_{ads} on O/Pt{111}⁴ has been reported to be negligible, this ion almost certainly arises from a surface methyl species. We note that oxygenated species such as O_{ads} and CH₃O_{ads} are suggested by the XPS experiments but are not directly detected in the SIMS measurements. The fact that only CH₃⁺ ions are observed with SIMS implies that CH₃ads does not decompose to CH_{n(n=0-2)} during the primary ion impact and ion ejection event. By 450 K the CH₃⁺ SIMS signal is no longer detected in agreement with previous TPD experiments¹² which show a CO thermal desorption peak denoting recombination and desorption of adsorbed carbon and oxygen. At no time during the decomposition of methanol are SIMS (or XPS) signals attributable to CO formation¹³ observed. This suggests that until 450 K, CO plays no part in the thermal decomposition mechanism of methanol adsorbed at 110 K on the Pd{111} surface.

The XPS results for this system are in agreement with the mechanism presented above with one addition. The carbon 1s

region for surface temperatures above 175 K reveals the presence of a methoxide adsorbate which is approximately equal in intensity to the methyl surface species. The carbon 1s photoelectron spectra for a 1.5 L CH₃OH exposure on Pd{111} at 110 K are shown in Figure 3a. The C 1s binding energy of 286.2 eV is that of methanol on Pd{111}.¹⁴ After heating the surface to 175 K the carbon 1s spectrum contains two peaks as shown in Figure 3b. The peak at 284.2 eV is consistent with a methyl species and the peak at 285.9 eV is assigned to the methoxide adsorbate. This assignment was determined by a comparison to methanol adsorbed on Pd{111} precovered with oxygen and heated to 175 K,¹⁴ a procedure known to produce methoxide.⁸ The presence of methoxide on clean Pd{111} is reasonable in our case since this species typically forms on an oxygen site, and an oxygen site is created, as OH_{ads}, every time CH₃OH dissociates at the C-O bond. It should be noted, however, that a mechanism wherein the methoxide is first formed, and then decomposes to methyl and hydroxyl, has not yet been ruled out. At 300 K the methyl and methoxide still exist on the surface, Figure 3c, but by 400 K the methoxide species has decomposed completely to CH₃ads as shown in Figure 3d.

In summary, we propose the following mechanism for the thermal decomposition of methanol on the Pd{111} surface from the evidence presented herein



The SIMS and XPS evidence suggests that methyl is an unusually stable adsorbate on the Pd{111} surface. The lack of C⁺, CH⁺, or CH₂⁺ SIMS signals at 400 K suggests that the methyl group is the only surface hydrocarbon present at this temperature. The fact that CH₄ and CH₃OH are¹⁵ the major hydrocarbon products from palladium catalysts is consistent with a mechanism wherein only CH₃ads can combine with H_{ads} or OH_{ads}.

Acknowledgment. We acknowledge the financial support of the National Science Foundation and the Office of Naval Research.

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(13) Experiments determining the SIMS spectra as a function of CO exposure revealed two trends. First the Pd⁺ signal was enhanced several orders of magnitude with exposures of <0.5 L CO. Second, a Pd(CO)⁺ peak was always detected, even at the lowest exposures. In the methanol decomposition experiments neither phenomena was observed.

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