

METHYL FORMATION FROM METHANOL DECOMPOSITION ON Pd{111} AND Pt{111}

Robert J. LEVIS, Jiang ZHICHENG and Nicholas WINOGRAD

The Pennsylvania State University, Department of Chemistry, University Park, PA 16802, U.S.A.

and

Sohail AKHTER and J.M. WHITE

University of Texas, Austin, Department of Chemistry, Austin, TX 78712, U.S.A.

Received 15 July 1988; accepted 30 September 1988

The decomposition of CH_3OH adsorbed on Pd{111} and Pt{111} is compared as the surface is heated between 100 and 500 K. Using secondary ion mass spectrometry (SIMS) and thermal programmed desorption (TPD) it is suggested that an anomalous CH_3^+ ion signal observed previously by Akhter and White on oxygen precovered Pt{111} arises from the formation of a surface CH_3 species resulting from activation of the C-O bond of CH_3OH . This interpretation stems from a recent observation by Levis, Zhicheng and Winograd that CH_3OH decomposes to CH_3 , OH and OCH_3 on clean Pd{111} between 100 and 300 K. The results are discussed in terms of the relative ability of these metals to synthesize CH_3OH from CO and H_2 .

Secondary ion mass spectrometry (SIMS) has recently been applied towards elucidating the surface chemistry of CH_3OH adsorbed on oxygen precovered Pt{111} [1] and clean Pd{111} [2] between 100 and 400 K. For both systems, the positive ion observed at m/e 15, assigned to CH_3^+ , is detected as a function of surface temperature and is related to the $\text{CH}_3\text{OH}_{\text{ads}}$ thermal decomposition reaction mechanism. Thermal programmed desorption (TPD) and SIMS studies of CH_3OH adsorbed on O/Pt{111} suggest that $\text{CH}_3\text{OH}_{\text{ads}}$ decomposes to $\text{CH}_3\text{O}_{\text{ads}}$ (methoxide) from 116 K to 140 K and that further heating causes decomposition to CO and H_2 . On Pd{111}, X-ray photoelectron spectroscopic (XPS) and SIMS measurements suggest that $\text{CH}_3\text{OH}_{\text{ads}}$ decomposes to $\text{CH}_{3\text{ads}}$, $\text{CH}_3\text{O}_{\text{ads}}$ and $\text{H}_2\text{O}_{\text{ads}}$ above 175 K, and that further decomposition to CO and H_2 occurs above 350 K. In light of the study, an anomalous increase in the CH_3^+ SIMS intensity vs. temperature plot for certain CH_3OH coverages reported in the Pt{111} investigation can be attributed to the formation of a CH_3 species. The production and stability of $\text{CH}_{3\text{ads}}$ on each surface may have implications in the relative catalytic properties of Pd and Pt based catalysts.

A critical contribution from the investigation on O/Pt{111} is that the transformation from $\text{CH}_3\text{OH}_{\text{ads}}$ to $\text{CH}_3\text{O}_{\text{ads}}$ can be detected using SIMS since the CH_3^+ intensity from $\text{CH}_3\text{OH}_{\text{ads}}$ is much larger than that from $\text{CH}_3\text{O}_{\text{ads}}$. This difference in fragmentation efficiency accounts for the pronounced decrease in the CH_3^+ SIMS signal in the temperature programmed (TP) SIMS spectrum shown in figure 1a, b and c between 110 and 140 K. During the TPSIMS experiment on Pt{111} an anomalous increase in the CH_3^+ signal is observed at 180 K. This signal vanishes at 220 K for initial CH_3OH exposures ≥ 0.12 L and does not reappear at temperatures at least up to 900 K. The anomalous increase was tentatively assigned to a change in the ionization probability of the CH_3^+ SIMS signal resulting from desorption of H_2O at 180 K.

On clean Pd{111} recent SIMS and XPS measurements of the CH_3OH thermal decomposition reaction from 110 K to 400 K have shown that $\text{CH}_{3\text{ads}}$, $\text{H}_2\text{O}_{\text{ads}}$ and $\text{CH}_3\text{O}_{\text{ads}}$ are formed with increasing surface temperature [2]. The XPS data, for example, show that there are two C 1s peaks of equal intensity formed at 175 K at 285.9 eV and 284.2 eV. The 285.9 eV peak is shown to arise from $\text{OCH}_{3\text{ads}}$ by comparison to the spectra for CH_3OH adsorbed on O/Pd{111} which is known to produce $\text{OCH}_{3\text{ads}}$ [4]. The 284.2 eV peak is assigned to $\text{CH}_{3\text{ads}}$. Although it is not possible to make this assignment from XPS data alone, we have shown that the intensity of this peak as a function of temperature correlates with the CH_3^+ ion observed in SIMS. The direct assignment of this CH_3^+ ion to $\text{CH}_{3\text{ads}}$ is possible for a number of reasons. First, a major source of CH_3^+ is from the ion-beam induced cracking of $\text{CH}_3\text{OH}_{\text{ads}}$. This species is gone from the surface by ~ 150 K and cannot contribute to the signal. Secondly, the CH_3^+ ion intensity derived from the ion-beam induced cracking of $\text{OCH}_{3\text{ads}}$ is found to be quite small on both Pt [1] and Pd [2,3]. Note, for example, that no increase in the CH_3^+ ion intensity is observed in figure 1c even though there is an extensive amount of $\text{OCH}_{3\text{ads}}$ formation [1]. Finally, it is possible that CH_3^+ ion signals could arise from recombination during desorption of $=\text{CH}_2$ or $\equiv\text{CH}$ surface species with H^+ . The CH_2^+ and CH^+ ion signals must also be present in this scenario. Since the SIMS result is conspicuously missing contributions from these fragment ions, we have concluded [2,3] that the only possible assignment for the large m/e 15 intensity and for the 284.2 eV C 1s peak after desorption and decomposition of CH_3OH is to $\text{CH}_{3\text{ads}}$.

With these assignments in hand, it is of value to compare the behavior of the m/e 15 peak for CH_3OH decomposition on Pd{111} to that found for Pt{111} between 110 and 400 K. For a 1 L CH_3OH exposure on Pd{111}, as shown in fig. 1d, the CH_3^+ SIMS intensity initially decreases between 110 and 150 K, once again indicating decomposition to $\text{CH}_3\text{O}_{\text{ads}}$. Above 150 K the CH_3^+ signal increases in a manner similar to the anomalous result on Pt{111}. The CH_3^+ intensity reaches a maximum at 200 K. The subsequent decrease between 200 and 300 K is due in part to a gradual removal of surface species, $\approx 15\%$ by 300 K, by the primary ion beam. On the Pd{111} surface the increase in the CH_3^+ signal is

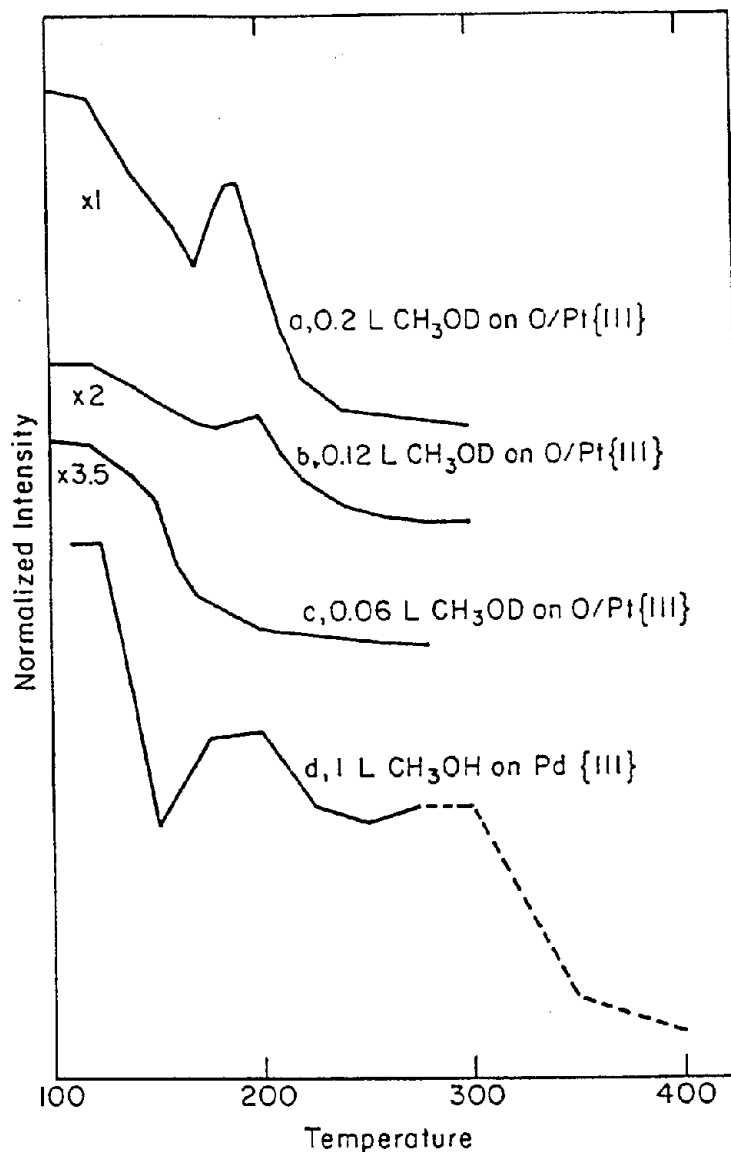


Fig. 1. Plots of the CH_3^+ ion intensity as a function of surface temperature for a) 0.20 L CH_3OD , b) 0.12 L CH_3OD , c) 0.06 L CH_3OD adsorbed at 100 K on 0.25 ML O on Pt{111}. The primary ion current was 1 nA and the heating rate was 1.1 K sec^{-1} . d) A plot of the CH_3^+ ion intensity as a function of temperature for a 1 L exposure of CH_3OH adsorbed at 110 K on Pd{111}. The dotted line is taken from an experiment of similar exposure at 130 K which was heated immediately to 273 K. For this plot, an entire SIMS spectrum is recorded, the temperature is then ramped 25 K and another spectrum is recorded. The primary ion current was 2.0 nA cm^{-2} and the beam energy was 3 keV.

not followed by the same substantial decrease at 220 K as on the Pt{111} surface. Rather, the CH_3 ion intensity slowly decreases until above 300 K, where $\text{CH}_{3\text{ads}}$ presumably begins to decompose to C_{ads} . Further heating to 300 K produces no change in the C 1s spectrum, while heating to 400 K causes the doublet of peaks at 285.9 and 284.2 eV to coalesce to a single peak at 284.3 eV, most likely attributable to C_{ads} . *The results on Pd{111}, which strongly suggest the formation and detection of $\text{CH}_{3\text{ads}}$ using SIMS, imply that the anomalous increase in the CH_3^+ signal on the O/Pt{111} surface between 180 and 220 K is also due to the formation of a CH_3 species.*

References

- [1] S. Akhter and J.M. White, *Surf. Sci.* 167 (1986) 101.
- [2] R.J. Levis, Z.C. Jiang and N. Winograd, *J. Am. Chem. Soc.* 110 (1988) 4431.
- [3] R.J. Levis, Z.C. Jiang and N. Winograd, in preparation.
- [4] J.A. Gates and L.L. Kesmodel, *J. Catal.* 83 (1983) 437.
- [5] J.L. Davis and M.A. Barteau, *Surf. Sci.* 197 (1988) 123.
- [6] S.R. Bare, J.A. Strocio and W. Ho, *Surf. Sci.* 155 (1985) L281.
- [7] J. Hrbek, R. De Paola and F.M. Hoffmann, *Surf. Sci.* 166 (1986) 361.
- [8] J.N. Russell, S.M. Gates and J.T. Gates, *Surf. Sci.* 163 (1985) 516.
- [9] B.A. Sexton, *Surf. Sci.* 102 (1981) 271.
- [10] I.E. Wachs and R.J. Madix, *J. Catal.* 53 (1978) 208.
- [11] C. Sudhakar and M.A. Vannice, *J. Catal.* 95 (1985) 227.
- [12] M.L. Poutsma, L.F. Elek, P.A. Ibaria, A.P. Risch, J.A. Rabo, *J. Catal.* 52 (1978) 157.