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

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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 $CH_3OH_{ads}$ thermal decomposition reaction mechanism. Thermal programmed desorption (TPD) and SIMS studies of $CH_3OH$ adsorbed on O/Pt{111} suggest that $CH_3OH_{ads}$ decomposes to $CH_3O_{ads}$ (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 $CH_3OH_{ads}$ decomposes to $CH_{3ads}$, $CH_3O_{ads}$ and $H_2O_{ads}$ 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 $CH_{3ads}$ 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 $CH_3OH_{ads}$ to $CH_3O_{ads}$ can be detected using SIMS since the $CH_3^+$ intensity from $CH_3OH_{ads}$ is much larger than that from $CH_3O_{ads}$. 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 $\geq 0.12$ 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 $CH_{3ads}$, $H_2O_{ads}$ and $CH_3O_{ads}$ 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 $OCH_{3ads}$ by comparison to the spectra for $CH_3OH$ adsorbed on O/Pd{111} which is known to produce $OCH_{3ads}$ [4]. The 284.2 eV peak is assigned to $CH_{3ads}$. 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 $CH_{3ads}$ is possible for a number of reasons. First, a major source of $CH_3^+$ is from the ion-beam induced cracking of $CH_3OH_{ads}$. 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 $OCH_{3ads}$ 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 $OCH_{3ads}$ formation [1]. Finally, it is possible that $CH_3^+$ ion signals could arise from recombination during desorption of $=CH_2$ or $\equiv CH$ 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 $CH_{3ads}$.

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 $CH_3O_{ads}$. 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, ≈ 15% by 300 K, by the primary ion beam. On the Pd{111} surface the increase in the $CH_3^+$ signal is

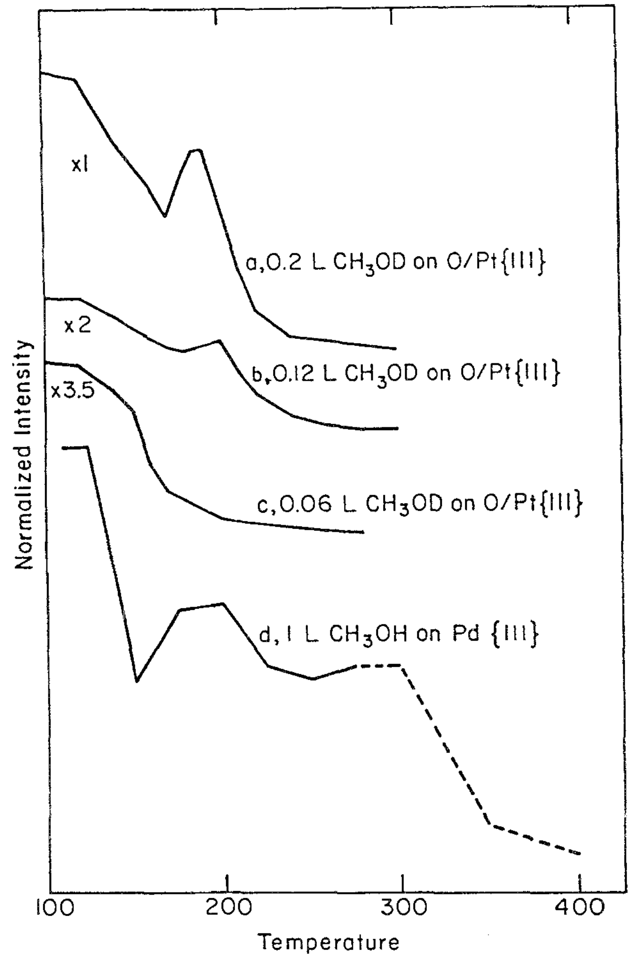

Fig. 1. Plots of the $CH_3^+$ ion intensity as a function of surface temperature for a) 0.20 L $CH_3OD$, b) 0.12 L $CH_3OD$, c) 0.06 L $CH_3OD$ adsorbed at 100 K on 0.25 ML O on Pt{111}. The primary ion current was 1 nA and the heating rated was 1.1 K sec$^{-1}$. d) A plot of the $CH_3^+$ ion intensity 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 $CH_{3ads}$ 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* $CH_{3ads}$ *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.*

The possibility of producing $CH_{3ads}$ on O/Pt{111} permits an interpretation of a second anomalous result in the TPSIMS spectra of the $CH_3^+$ ion on O/Pt{111}. The increase in the $CH_3^+$ intensity between 180 K and 220 K shown in fig. 1a, b and c demonstrate a dependence on the initial $CH_3OD$ exposure. The amount of the anomalous $CH_3^+$ intensity is proportional to the $CH_3OH_{ads}$ to $O_{ads}$ ratio, or put another way, increasing the $CH_3OD$ exposure increases the amount of $CH_3^+$ ion observed between 180 K and 200 K. This suggests that a certain amount of $CH_3OD_{ads}$ will titrate all of the available O sites, and that excess $CH_3OD_{ads}$, possibly bound to clean Pt sites, will then dissociate at the CO bond to form $CH_{3ads}$ and $OD_{ads}$. This is consistent with the notion that O sites enhance the formation of $CH_3O$ [5–10] and with the result on Pd{111} suggesting that the clean surface may promote the activation of the methanolic CO bond. A similar titration of the O sites on O/Pd{111} is suggested by an inverse relationship between the C 1s XPS signal at 284.2 eV, which denotes $CH_{3ads}$ formation, and the initial O coverage [3].

In conclusion, we consider the relative stability of the $CH_3$ species on Pt{111} and Pd{111}. The $CH_3$ adsorbate decomposes at 220 K on the Pt{111} surface while on the Pd{111} surface the adsorbate is stable at least until 325 K. The XPS and SIMS experiments on the decomposition of $CH_3OH$ on O/Pd{111} [3] demonstrate that once formed, the $CH_3$ adsorbate has a stability which is virtually identical to $CH_{3ads}$ on the clean surface. This suggests that the decomposition temperature for $CH_{3ads}$ formed on O/Pt{111} approximates that found on the clean Pt{111}. We conclude that the $CH_3$ species is not as stable on Pt{111} as on Pd{111} which may correlate to the relative catalytic properties of these two metals. A stabilized $CH_{3ads}$ hydrocarbon fragment on the Pd{111} surface may explain the ability of pure Pd catalysts [11] to produce only $CH_3$ containing species such as $CH_3H$, $CH_3OH$, $CH_3CH_3$, and $CH_3OCH_3$ from CO and $H_2$ feed gases from the combination of $CH_{3ads}$ with $H_{ads}$, $OH_{ads}$ $CH_{3ads}$ and $OCH_{3ads}$, respectively. In addition, the lower stability of the $CH_3$ fragment on the Pt surface may correspond with the order of magnitude lower $CH_3OH$ production rate on Pt catalysts when compared to Pd catalysts [12]. It would be of interest to use SIMS to determine the relative thermal stability of the methyl adsorbate on Ir{111}, which is comparable to Pt in $CH_3OH$ production [12], and Ni{111}, which produces no $CH_3OH$ from CO and $H_2$ precursors. We believe that the combination of SIMS with quantitative surface techniques is particularly powerful for the pursuit of relatively complex adsorbate/metal decomposition mechanisms.

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