

Secondary Ion Mass Spectrometry

SIMS VI

**Proceedings of the Sixth International Conference on
Secondary Ion Mass Spectrometry (SIMS VI)**

Palais des Congrès, Versailles, Paris, France
September 13–18th, 1987

Editors

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AN ULTRAHIGH VACUUM STUDY OF THE
PRODUCTION OF METHANOL ON Pd{111}

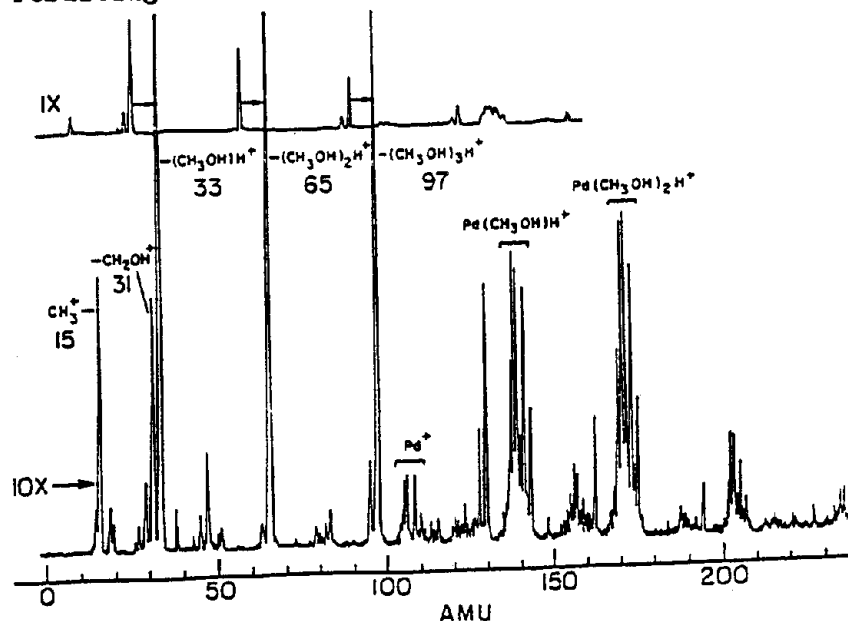
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Surface analytical techniques capable of characterizing molecular surface species are necessary for understanding the surface reactions pertaining to heterogeneous catalysis. While a tremendous amount of research has been directed towards understanding the mechanism of CH_4 production from synthesis gas (1), almost no work has been focused toward understanding the production of CH_3OH . Palladium metal is unique in its alcohol producing ability (2). In order to gain insight into the surface chemistry of CH_3OH on Pd, we have adsorbed CH_3OH , CH_3OD , CD_3OD , CO , O_2 , and H_2 onto the Pd{111} face under various conditions using static SIMS to analyze the resulting surface chemistry.

The mechanism proposed herein is a consequence of three basic experiments. The first is a series of low temperature, 110K, methanol (CH_3OH , CH_3OD and CD_3OD) exposures aimed at determining predominant surface species. The second is a series of coverage and/or temperature dependent exposures of methanol on Pd{111} providing information about the relative stabilities and concentrations of the surface species. Finally there is a series of CO , O_2 , H_2 , and CH_3OH control experiments characterizing the effects of the resulting adsorbates on the SIMS results.

Fig. 1
SIMS spectra
for 10L. CH_3OH
on Pd{111}
at 110K



Results:

A SIMS spectrum taken after a 10 Langmuir (L) exposure of CH_3OH at 110K on Pd{111} is shown in Figure 1. The series of peaks at 33, 65, and 97 atomic mass units (amu) corresponds to hydrogenated CH_3OH clusters. A series of $\text{Pd}(\text{CH}_3\text{OH})_n\text{H}^+$ $n=1,2,\dots$ are also apparent. In addition to the CH_3OH clusters, a peak at 31 amu, signifying $(-\text{CH}_2\text{OH})^+$ is observed as well as a methyl $(-\text{CH}_3)^+$ species at 15 amu. Unlike previous SIMS catalytic studies (3,4), the carbon, methylidyne and methylene species are not present in great quantity. Even though a slight methylene peak is observed, no significant decomposition of the methyl species during the sputter event is observed. As noted in Table 1, the expected amu shifts are observed when the deuterated analogues are used.

Table 1 Surface species observed using isotopes of methanol

Dose Gas	(Methyl)	(Hydroxymethyl)	(Methanol)H
CH_3OH	$-\text{CH}_3^+$ 15	$-\text{CH}_2\text{OH}^+$ 31	$-(\text{CH}_3\text{OH})\text{H}^+$ 33
CH_3OD	$-\text{CH}_3^+$ 15	$-\text{CH}_2\text{OD}^+$ 32	$-(\text{CH}_3\text{OD})\text{D}^+$ 35
CD_3OD	$-\text{CD}_3^+$ 18	$-\text{CD}_2\text{OD}^+$ 34	$-(\text{CD}_3\text{OD})\text{D}^+$ 38

The change in the methyl, hydroxymethyl, and methanol intensities is plotted against increasing CD_3OD exposure in Figure 2. The plot reveals that $-\text{CD}_3^+$ is the first observable surface species. This rules out the possibility that the methyl group is an ion induced decomposition product of another surface species formed between 1 and 3L exposure. At 3L exposure, the $(\text{CD}_3\text{OD})\text{D}^+$ species is the most intense while the $(\text{CD}_2\text{OD})^+$ species remains the least intense. Above 5L exposure, an overlayer of methanol forms. Subsequently, the $(\text{CD}_3\text{OD})\text{D}^+$ species is the most

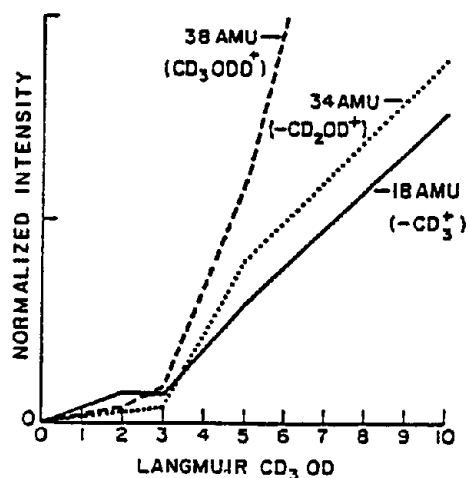


Fig.2 Adsorbate Ion Intensity vs. CD_3OD exposure

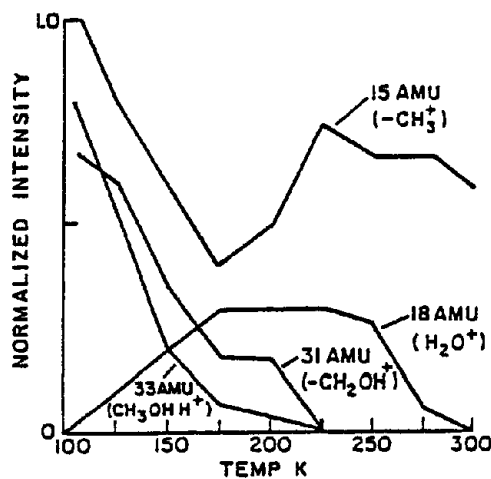
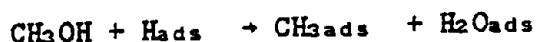


Fig.3 Adsorbate Ion Intensity vs. Temperature for 4 L. CH_3OH .

intense peak and the $(CD_3)^+$ species is the least intense. The fact that the $(CD_3OD)D^+$ peak increases at three times the rate of the $(CD_2OD)^+$ or the $(CD_3)^+$ peak suggests that as the overlayer forms the ion-induced decomposition of methanol decreases.

The change in the $(CH_3)^+$, $(CH_2OH)^+$, $(CH_3OH)H^+$, and H_2O^+ intensities is plotted against temperature in Figure 3 for a 4L exposure of CH_3OH at 110K on the Pd{111} surface. Between 110K and 175K all of the hydrocarbon signals decrease. This decrease is partially due to the desorption of CH_3OH , as noted by an increase in background pressure, and partially due to the decomposition of CH_3OH , as noted by the appearance of an $(H_2O)^+$ signal. At 175K the $(H_2O)^+$ peak reaches a maximum and the $(CH_3)^+$ peak begins to increase. At 225K the methyl $(CH_3)^+$ peak reaches a maximum and the $(CH_2OH)^+$ and $(CH_3OH)H^+$ peaks disappear. Upon heating further, the $(CH_3)^+$ peak decreases slowly to vanish at 500K while the $(H_2O)^+$ peak decreases to vanish at 275K. Because no $(PdCO)^+$ signal is detected at any time during the experiment, we propose the following methanol decomposition mechanism:



The control experiments involving the adsorption of CO and O_2 agree with the previously published results (5,6), specifically, a dramatic increase is observed in the Pd^+ secondary ion yield with minimal exposure. Finally, the adsorption of methanol at 300K produced the following signals: $(C)^+$, $(CH)^+$, $(CH_2)^+$, $(CH_3)^+$, $(O)^+$, and $(OH)^+$ while no evidence for $(PdCO)^+$, $(CH_2OH)^+$, $(OCH_3)^+$, or $(CH_3OH)H^+$ was observed.

Conclusions:

- 1) Methanol decomposes to CH_3ads and H_2O_{ads} on the Pd{111} surface with no evidence for CO formation.
- 2) Methanol is not stable on the Pd{111} surface above 175K.
- 3) Methyl ($-CH_3$) is the first stable adsorbate at 110K and the only stable adsorbate at 300K on the Pd{111} surface.
- 4) Methyl ($-CH_3$) suffers no ion beam decomposition.

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