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## DISCLAIMER

## ABSTRACT

High resolution electron energy loss spectroscopy has been used to study the decomposition of methanol on a Pt(111) surface. Several intermediate states in the decomposition are identified by quenching the sample when reactions occur. At 100 K a set of peaks at 800, 1040, 1350, and 2890 $cm^{-1}$ indicates the presence of a multilayer molecularly adsorbed methanol. As the sample is warmed to 130 K peaks develop at 1700 and 2780 $cm^{-1}$, suggesting the formation of formaldehyde on the surface. With further heating, peaks grow at 1820 and 2560 $cm^{-1}$ due to the formation of a formyl species. This marks the first reported observation of a formyl species during the decomposition of methanol over Pt (111). Further heating leads to the final conversion of the surface species to adsorbed CO and carbonaceous residues.

# INTRODUCTION

Many studies of the adsorption of methanol have been carried out on single crystal surfaces in an effort to understand the production of methanol from carbon monoxide and hydrogen. A methoxy intermediate has been identified on a number of clean metal surfaces, including Cu [1], Ni [2], and Ag [3]. It has been shown that the methoxy species is stable on oxygen covered surfaces of Ni [4], Ag [5], Pt [6], and Pd [7].

Two mechanisms have been proposed for methanol synthesis from carbon monoxide and hydrogen [8] . The first is the hydrogenation of an adsorbed carbon monoxide molecule to form an adsorbed formyl intermediate, which then undergoes successive hydrogenation to form methanol as presented in Fig. 1. The second mechanism involves the insertion of carbon monoxide into an adsorbed hydroxyl species to form an adsorbed formate species, as indicated in Fig. 2. This surface formate undergoes further hydrogenation and dehydration to form a surface methoxy species and finally methanol. There is a significant difference in these two mechanisms which lies in the way the intermediates interact with the surface. In the first case the bonds to the surface are formed through the carbon atom. The hydrogenation then takes place while preserving the surface carbon bond. In the second mechanism the CO bonded to the surface reacts with a surface

hydroxyl to form formate with the surface oxygen bond being preserved.

While there have been a large number of studies on the decomposition of small oxygen containing molecules, there has been no observation to date of the formyl species. Yates [9] specifically tried to find this species on Rh but without success. The observation of this species as a functional group in model organic compounds clearly demonstrates its existence [10], but this work includes the first reported observation of a formyl species formed during the decomposition of methanol over Pt(111).

## EXPERIMENTAL

The experiments were conducted in a surface analytical chamber which will be described in detail elsewhere [11]. The system consists of an ultrahigh vacuum (UHV) chamber equipped with low energy electron diffraction (LEED) optics, which are also used for Auger electron spectroscopy (AES), a quadrupole mass spectrometer, and a high resolution electron energy loss spectrometer (HREELS).

The Pt(111) sample was spark cut from a single crystal rod and x-ray oriented to within $1^{\circ}$. The sample was polished using standard metallurgical techniques which were followed by chemical etching. The crystal was mounted in the UHV system by spot-welding from the back to two thin platinum foils, which serve as

a mechanical support for the assembly as well as a thermal linkage to a liquid nitrogen heat sink on the manipulator. The crystal temperature may be varied between 100 K and 1300 K and is monitored by a chromel alumel thermocouple attached to the side of the crystal.

The surface was cleaned by argon bombardment to remove traces of calcium and silicon. Carbon was removed by heating the crystal to $900^{\circ}C$ in an oxygen atmosphere. The surface was then flashed to $1200^{\circ}C$ for a final anneal and to desorb any residual oxide sublayer. This procedure was checked by AES and LEED, revealing a clean and well ordered surface.

The HREELS spectrometer is based on a design by Sexton [12] and consists of two $127^{\circ}$ cylindrical electrostatic deflectors mounted in a fixed configuration on a 10 in. flange. The spectrometer is operated at a resolution of about 10 meV for primary electrons of 5 eV to 7 eV energy and a sample current of the order of $10^{-10}$ amps.

The sample manipulator played a major role in the ability to perform most of the experiments using thermal cycling and thermal quenching. The design is based on a differentially pumped O-ring sealed rotary feedthrough, described by Yates et al. [13], which is bolted to a bellows sealed X-Y-Z-tilt translational stage. A very simple cryostat, a stainless steel tube with a copper base, is bolted to the top flange of the rotary insert. Cooling liquid, usually liquid nitrogen, is poured or pumped directly into the tip of the cryostat. The sample holder is a 1/4 inch thick,

1 inch wide plate of OFHC copper bolted directly to the cryostat
bottom. The mounted sample is bolted to the end of this plate.
The sample is heated by radiation and electron bombardment from a
filament mounted behind the sample in a cutout of the plate. The
heater assembly is thermally isolated from the rest of the sample
holder with ceramic spacers. Samples can be cooled at a rate of
4-10 K per second.

Each experiment begins by cooling the sample to liquid
nitrogen temperature and dosing it with the desired gas.  The
HREELS spectrum of the resulting structure is taken.  The sample
is then slowly warmed. Reactions are identified by monitoring the
intensity of the HREELS elastic peak, which is continuously
displayed on an oscilloscope. Any change in the chemical struc-
ture of the adsorbate usually leads to a change in the elastic
peak. The intermediate states found in this manner are frozen
using the fast cooling capability of the manipulator and are
identified by the appearance of new vibrational modes.

## RESULTS

Figures 3 and 4 show a typical sequence of HREELS results
for the adsorption and thermal evolution of $CH_3OH$ over Pt(111).
Table 1 presents the frequency assignments for the loss struc-
tures in this set of experiments.

Spectrum 3a shows the loss pattern for bulk methanol with
the presence of a strong $O-CH_3$ stretch at 1060 $cm^{-1}$.  The $CH_3$

symmetric and degenerate stretch, in the high energy loss portion

of the spectrum (2800 $cm^{-1}$, 2980 $cm^{-1}$) indicates a possible

tilted configuration for the molecules.  Fig. 3b also shows the

3200 $cm^{-1}$ shoulder corresponding to the OH stretch and the

1460 $cm^{-1}$ peak representing contributions from the OH bending and

$CH_3$ deformations.  The low energy region is not well charact-

erized due to the superposition of several different modes like

Pt-O stretching and bending, rocking of the entire molecule, and

CO torsion.  We also observed that at this stage the elastic peak

has a FWHM of 15 mV to 18 mV with a broader base and a large

tail extending into the background.  This is probably caused by

the amorphous-like layer structure of the adsorbate.

Heating this surface to 120 K causes some of the film to

desorb and a second intermediate state appears, Fig. 3c.  The

elastic peak is almost back to its original FWHM and its intens-

ity is strongly improved ($10^4$ cps).  This increase in

reflectivity represents an increase in the order of the $CH_3OH$

overlayer, which can be confirmed by the overall decrease in

background and better resolution of individual peaks.  The loss

pattern is generally the same as the previous set, but the 1460

cm-1 peak now has a clear shoulder at 1700 $cm^{-1}$.

Further annealing of this film to 130 K leads to a surface

structure with the loss spectrum of Fig. 3d.  At this point there

is probably no more than a monolayer of the adsorbate on the sur-

face. The count rate for the elastic peak is similar to that for

the original bare platinum surface.  The loss spectrum is now

characterized by a strong methoxy species at 1040 $cm^{-1}$, with a well defined low energy peak at 560 $cm^{-1}$, and a small OH shoulder at 3150 $cm^{-1}$. The $CH_3$ stretch region is now multistructured which may be an indication of the coexistence of different $CH_x$ species. The 1460 $cm^{-1}$ peak is still present but the previous shoulder has developed into a strong peak at 1720 $cm^{-1}$. This last structure will be the key to interpretation of this reaction.

The next spectrum (3e) shows a marked activity on the surface represented by the splitting of the 1720 $cm^{-1}$ region into two structures, the beginning of the CO formation with a loss peak at 2080 $cm^{-1}$, a series of pre-shoulders at 2960 $cm^{-1}$ region, and the near disappearance of the high energy OH stretch. The methoxy peak is very well defined and the low energy structure is becoming more shoulder-like. This can be an indication of the start of poisoning of the surface by a carbonaceous layer.[14]

Fig. 4f shows the next step in the annealing process begun in Fig. 3. The dominant features are the 1800 $cm^{-1}$ peak, a strong CO peak at 2080 $cm^{-1}$ and a clear structure at 2560 $cm^{-1}$. The $CH_3$ band seems to have lost its individuality of symmetric and degenerate peaks, which can be an indication of a more upright positioning of the O-$CH_3$ species on the surface. The 140 $cm^{-1}$ peak is decreasing in intensity and becoming broader.

Upon further annealing this surface structure starts to convert into a CO covered surface as shown in Fig. 4g. The major peaks are still present: the methoxy 1040 $cm^{-1}$, the formyl

1800 cm$^{-1}$, the CH and CH$_x$ modes at 2780 cm$^{-1}$ and 2960 cm$^{-1}$, and the Pt-C and Pt-CO at 500 cm$^{-1}$ and 2080 cm$^{-1}$. The final stage is the complete conversion of this structure into a CO overlayer, presented in Fig. 41. The 1800 cm$^{-1}$ shoulder on the 2080 cm$^{-1}$ CO peak has disappeared and the low energy end of the elastic peak is characterized by a long tail in the 400 cm$^{-1}$ to 600 cm$^{-1}$ region characteristic of a carbon poisoned surface.

The same experiment was performed with CD$_3$OD (d-methanol) adsorbed on a clean Pt(111) surface. The changes in the corresponding vibrational frequencies due to the deuterium mass effect help in assigning the major loss peaks. The loss spectrum for the overall reaction is characterized by an extensive exchange of deuterium and hydrogen, with the CD$_x$ and CH$_x$ bands clearly distinguishable. In the same temperature range of 130 K to 150 K there appears a 1700 cm$^{-1}$ d-formaldehydic loss peak. With further temperature increase this peak splits and changes to include a structure at 1800 cm$^{-1}$ corresponding to a deuterated formyl surface species. From this point on, the thermal development of the reaction follows the same pattern presented for CH$_3$OH.

LEED studies were done on the Pt(111)/CH$_3$OH system, but caution must be exercised when analyzing the data. The LEED electron beam can irreversibly damage the overlayers. The multilayer structure is characterized by a large increase in background, with no significant ordering. Annealing to higher temperatures brings back a sharper (1x1) pattern and a lower

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background. In most cases no intermediates were detected with LEED as extra structures or spots, which seems reasonable assuming a large instability under the electron beam as well as possibly very low coverage for these radicals.

Auger spectra were also taken but were always marked by a strong decomposition of the adsorbed film under the electron beam resulting in a small carbon signal independent of the apparent thermal reaction stage.

## DISCUSSION

Based on the data from these experiments the proposed model for the adsorption and decomposition of methanol over clean platinum can be represented as follows. In large doses methanol is adsorbed in a bulk form generating an amorphous film with no preferred orientation. All of the major infrared frequencies reported in the literature [14] can be seen in the spectrum. The second stage shows this multilayer desorbing, leaving a monolayer structure on the surface. The presence of a strong 1040 cm$^{-1}$ O-CH$_3$ stretch vibration indicates a predominant adsorbed methoxy species. This peak is broader than expected, suggesting island formation and agglomeration in slightly different adsorption sites with strong intramolecular hydrogen bonding. The presence of the two forms of CH$_3$ vibrations, symmetric and degenerate, seems to indicate that this methoxy species is preferentially tilted with respect to the surface. This stage still shows a

small presence of an OH stretch band at 3200 cm$^{-1}$. There are probably residues of bulk methanol in 3-D islands due to the rapid quenching.

In the decomposition sequence of Figures 3 and 4, the major feature is the appearance of a peak at 1720 cm$^{-1}$ that moves to 1800 cm$^{-1}$ with increasing temperature. The major CO decomposition product forms at the same time. The 1720 cm$^{-1}$ peak together with the shoulder at 2870 cm$^{-1}$ indicates the formation of a formaldehydic structure of the type Pt-OCH$_2$ generated by donation of a hydrogen atom to the platinum metal or into the recombination process for the desorption of the remaining OH species into water. This formaldehydic surface species will assume a more bridged position with the pseudo bonding of the carbon to the surface, generating a meta-structure of the type Pt-CH$_2$O-Pt. This is shown by the splitting of the 1720 cm$^{-1}$ peak and consequent shifting to higher energies. With the temperature increase, this structure is presented with several pathways for stabilization: formation of carbon monoxide, dissociation into adsorbed carbon and oxygen, recombination with adsorbed hydrogen, formyl formation, and processes involving other less stable radicals. All these features seem to be represented in the spectra in the temperature range of 130 K to 150 K. The formyl species is characterized by the two loss peaks at 1800 cm$^{-1}$ and 3140 cm$^{-1}$. The formation of this radical is favored by the backdonation of the platinum d-electrons to the pseudo-sigma orbital of the bridged CO, with the compensating charge flow from

the Pt-O bond, and consequent weakening of the previous formald-
ehydic configuration and final alignment of the Pt-CHO radical.
This formyl species is finally decomposed and or desorbed at
higher temperatures, possibly by bond breaking and dehydrogena-
tion to form a thermally stable CO. The series of intermediates
found during this process, most importantly the appearance of a
formyl species, favors the methanol synthesis mechanism described
in Fig. 1 over that shown in Fig. 2.

## ACKNOWLEDGEMENTS

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## Figure Captions

Fig. 1    One mechanism proposed [8] for the formation of
         methanol through hydrogenation of CO.

Fig. 2    An alternate mechanism proposed [8] for the formation
         of methanol through the insertion of a surface
         hydroxyl on the CO and further hydrogenation and
         dehydration.

Fig. 3    HREELS sequence of methanol adsorption over Pt(111) and
         thermal reaction from $T \approx 100$ K to $T \approx 135$ K. All
         spectra are taken after recooling to 100 K.

Fig. 4    Continuation of Fig. 3 showing the HREELS spectra as the
         temperature is raised from 140 K to 200 K. All spectra
         are taken at 100 K.

CO

↑

* = C = O    H⁻ + H⁺ ↑

$$* = C = O$$

with H⁻ + H⁺

↑

$$\underset{H}{\overset{O}{\|}}C-*$$

H⁻ + H⁺ ↑

$$\underset{H}{\overset{OH}{|}}C-*$$

H⁻ + H⁺ ↑

$$\underset{H}{\overset{OH}{|}}\underset{}{\overset{H}{|}}C-*$$

H⁻ + H⁺ ↑

$$CO \longrightarrow CO\text{-}* \quad OH\text{-}* \longrightarrow \underset{\overset{\displaystyle\|}{O}}{H-C}-O\text{-}* + 2\,\overset{H}{|}\text{-}* \longrightarrow \underset{\overset{|}{O}\text{-}*}{CH_2OH} \xrightarrow{-H_2O} + 2\,\overset{H}{|}\text{-}* \longrightarrow CH_3\text{-}O\text{-}* + \overset{H}{|}\text{-}*$$

x1000

INTENSITY (Arbitrary Units)

T=100°K  a

T=120°K  b

T=125°K  c

T=130°K  d

T=135°K  e

0    1000   2000   3000   4000
ENERGY LOSS (cm⁻¹)