DECOMPOSITION OF $H_2CO$ AND $CH_3OH$ ON Ru(110) AND Ni(100)

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Abstract: The coadsorption of $H_2 + CO$ as well as the adsorption and decomposition of $H_2CO$ and $CH_3OH$ on Ru(110) and Ni(100) have been studied using temperature programmed desorption methods. CH$_4$ is observed as a minor product in the thermal decomposition of $H_2CO$ on Ru(110), but is not detected as a desorption product from the other adsorbate-substrate combinations. The results suggest that oxygenated hydrocarbon complexes may be of importance in the catalytic methanation reaction on Ru surfaces, but not on Ni surfaces.

INTRODUCTION

Both Ru and Ni are active catalysts for the hydrogenation of CO to produce CH$_4$. This reaction has long been suspected to proceed by mechanisms involving surface intermediates such as HCO(ads) or HCOH (ads) /1/. In order to investigate these possibilities, we have studied the chemisorptive behavior of H$_2CO$ and CH$_3OH$ on single crystals of Ru and Ni. Temperature programmed desorption (TPD) was employed, using a quadrupole mass spectrometer (QMS) to determine product yields and desorption kinetics. In addition, thermal desorption from pure hydrogen and pure CO layers, and from coadsorbed layers of $H_2 + CO$ has been studied on Ni(100).

EXPERIMENTAL PROCEDURES

The Ru single crystal disk, cut and polished to expose Ru(110) faces on both sides, could be electrically heated from 300 K - 1600 K using a.c. current. The crystal was cleaned repeatedly at 1515 K in O$_2$ at $10^{-9}$ Torr, followed by heating in vacuo at 1515 K. In agreement with previous work, this yields a clean Auger spectrum /2,3/. The Ni crystal disk exposed (100) faces; it could be electrically heated from 77 K - 1400 K. Cleaning was achieved by repeated heating at 1400 K in O$_2$ at $1 \times 10^{-7}$ Torr, followed by reduction of both faces at 1400 K in a H$_2$ beam at $2 \times 10^{-4}$ Torr. Auger spectroscopy indicated the Ni was clean, in agreement with previous results /4/.

Adsorbate molecules were deposited on both faces of the crystals using a symmetrical collimated molecular beam doser /3/. Following adsorption, the crystal was rotated to the region of the QMS,

Table I. Desorption Products from Adsorbates on Ru(110) and Ni(100)

<table>
<thead>
<tr>
<th>Relative Desorption Yield Magnitude</th>
<th>$H_2CO$</th>
<th>$CH_3OH$</th>
<th>$H_2CO$</th>
<th>$CH_3OH$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ru(110)</td>
<td>Ru(110)</td>
<td>Ni(100)</td>
<td>Ni(100)</td>
</tr>
<tr>
<td>100%</td>
<td>CO</td>
<td>CO</td>
<td>CO</td>
<td>CO</td>
</tr>
<tr>
<td>2 - 10%</td>
<td>H$_2$</td>
<td>H$_2$</td>
<td>H$_2$</td>
<td>H$_2$</td>
</tr>
<tr>
<td>~ 0.1%</td>
<td>H$_2CO$</td>
<td>CH$_3OH$</td>
<td>H$_2CO$</td>
<td>H$_2CO$</td>
</tr>
<tr>
<td></td>
<td>CO$_2$</td>
<td>H$_2CO$</td>
<td>CO$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$_2$</td>
<td>H$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_4$</td>
<td>CO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>limit of detectability of CH$_4$(15)</td>
<td>0.01%</td>
<td>&lt; 0.05%</td>
<td>.01%</td>
<td>0.1%</td>
</tr>
</tbody>
</table>
and the TPD of various products was monitored at reduced pumping speed. Base pressures were near 2 x 10^{-10} Torr.

RESULTS

Table I shows a comparison of the desorption product yields from H_2CO and CH_3OH adsorbates (saturation 300 K-coverages) on Ru(110) and Ni(100). The yields were measured by integration of TPD peaks and are reported in a semi-quantitative fashion without correction for relative QMS sensitivities or pumping speed differences of the various molecular weight products. Depending upon the adsorbate and its influence on experimental vacuum conditions, the lower limit of sensitivity ranges between 10^{-3} and 10^{-2} of the CO yield. Desorption spectra and yield measurements as a function of coverage will be reported elsewhere for H_2CO and CH_3OH adsorbates /3,5,6/. Desorption measurements involved the following mass peaks for each product, with cross checks between mass 31 and mass 15 to separate CH_3OH from CH_4 desorption: CO(28); H_2(2); H_2CO(30); CH_3OH(31,15); CH_4(15 corrected to equivalent 16 yield); H_2O(18); CO_2(44).

An interesting comparison of TPD behavior for pure hydrogen, pure CO, and coadsorbed mixtures on Ni(100) produced at 77 K is shown in Fig. 1. Coadsorbed layers were produced by exposure of a saturated H-layer to various CO exposures and an unusual interaction between the two adsorbates was observed in which simultaneous desorption of H_2 and CO occurs. For coadsorbed layers of H_2 + CO, no yield of organic products was observed on Ni(100) or Ru(110)/3/. Furthermore, when either Ru(110) /3/ or Ni(100) /6/ was exposed to a 4:1 H_2/CO mixture at an incident beam pressure of 10^{-3} Torr, no yield of CH_4 was observed in the crystal temperature range of 300 K to 1400 K; the sensitivity of this measurement is 1 x 10^{-6} of the local H_2 + CO pressure. This indicates that severe kinetic limitations exist for the methanation reaction at low pressures, as would be expected from extrapolation of the reaction rates measured at much higher H_2 + CO pressures /12/.

DISCUSSION

A. Interaction of H_2CO and CH_3OH with Transition Metals

The basic idea behind the selection of H_2CO or CH_3OH as adsorbates on Ru or Ni was to test whether these molecules would yield CH_4 upon thermal desorption in contrast to the zero (or measurably low) yield of CH_4 from coadsorbed hydrogen and CO. Thus, surface complexes derived from adsorbates containing O-C-H bonding might yield CH_4 through consecutive surface reactions in which the C-O bond is broken as multiple C-H bonds form.

Other XPS or molecular beam studies of H_2CO or CH_3OH suggest however, that the dominant surface processes occurring during adsorption at 300 K on Ru /3,5/, Ni /6,7/, or W/8,9/ is the decomposition of the organic molecule to produce hydrogen and CO. Surface concentrations of any surface complexes formed at 300 K are low, and CH_4 yields are correspondingly low. A summary of results regarding CH_4 production for all systems so far studied is given in Table II.

Table II suggests that species derived from H_2CO may play a role in the methanation reaction on Ru /1,12/ and W /11/. It is also possible, however, that the mechanism for CH_4 formation from H_2CO-derived complexes bears little or no relation to the mechanism for CH_4 formation from H_2 and CO at high pressures and further experiments will be required to clarify this. A mechanism involving HCO(ads) as an intermediate in the methanation reaction on W has been proposed /9/ and investigated /13/. Recent theoretical work /14/ suggests that HCO(ads) is an energetically favored species.

We have no evidence at present that species derived from CH_3OH play a role in CH_4 synthesis on Ru or Ni.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Ru(110)(3,5)</th>
<th>Ni(100)(6)</th>
<th>W(100)(8-10)</th>
<th>W(111)(8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2CO</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>CH_3OH</td>
<td>-</td>
<td>-</td>
<td>+ (10)</td>
<td></td>
</tr>
</tbody>
</table>
The absence of observable CH₄ production from H₂CO or CH₃OH on Ni(100) suggests that oxygenated hydrocarbon complexes may not be of importance in the methanation reaction on Ni surfaces. This is in accord with recent results suggesting that a carbonaceous intermediate may be of importance on Ni /15, 16/.

B. Interaction of H(ads) and CO(ads) on Ni(100)

As shown in Fig. 1, an unusual interactional effect was observed on Ni(100) when a saturated H(ads) layer at 77 K was exposed to CO. The CO induces the formation of a new H₂ desorption state (Σ) and itself populates a new CO state (Σ). The onset temperature of desorption of H₂ and CO from their Σ states is ~196 K in both cases. The Σ states are observed to form at equivalent CO exposures and they develop monotonically together. These observations suggest that both Σ states originate from a similar source which yields desorbing H₂ and CO. While this could be due to the formation of a new molecular complex (such as HCO(ads), etc.), we believe in agreement with Conrad, et al. /17/ that it is more reasonable to consider the interaction to involve H(ads) and CO(ads) since Σ states are not produced from H₂CO or CH₃OH adsorbates on Ni(100). Correlated desorption of Σ-H₂ and Σ-CO may be viewed as a cooperative effect in

TEMPERATURE PROGRAMMED DESORPTION FROM Ni(100)

Fig. 1. Temperature Programmed Desorption from Ni(100)

Pure Adsorbates
A. H₂ exposures range from < 1 L to 17 L
C. CO exposures range from 0.2 L to 7 L

Mixed Adsorbates
B. 17 L H₂ exposure + 1 L-CO; 2 L-CO; 3 L-CO; 8 L-CO; 17 L-CO.
D. 17 L H₂ exposure + 1.2 L-CO; 1.8 L-CO; 2.4 L-CO; 3 L-CO; 8 L-CO; 17 L-CO.
1-L = 10⁻⁶ Torr sec.
the interacting layer. For example, CO could stabilize a species indicated schematically as

\[ \begin{array}{c}
\text{Ni} \\
\text{H} \\
\text{Ni} \\
\text{H} \\
\text{Ni} \\
\end{array} \]

in which the H...H separation is small compared to the spacing in a pure H(ads) layer. Desorption of CO could lead to recombination of neighbor H atoms leading to H desorption rather than a return to normal H(ads) bonding. A process of this general type would produce a close correlation between $\Sigma$ -H$_2$ and $\Sigma$ -CO evolution and is consistent with the first order kinetics for $\Sigma$ -H$_2$ and $\Sigma$ -CO evolution indicated by the constancy of the peak desorption temperature with increasing coverage. This unusual interaction deserves detailed study by various spectroscopic means in order to more fully understand its character.

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REFERENCES

/7/ T.Dickenson and R.Madix (to be published).


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