The adsorption and decomposition of methanol on the Rh(100) surface

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The adsorption and decomposition of methanol on the Rh(100) surface have been studied using high-resolution electron energy loss spectroscopy and thermal desorption mass spectrometry. Below 200 K, methanol is molecularly adsorbed and bonds to the surface via the oxygen atom. At 200–220 K, a saturated methanol layer undergoes two competing reactions: desorption and OH bond cleavage to form an O-bonded methoxy species. The methoxy species is stable to approximately 250 K. Between 250 and 320 K, a fraction of the methoxy species decomposes to form coadsorbed CO and hydrogen adatoms while the remainder recombines with hydrogen adatoms to desorb as molecular methanol. The hydrogen adatoms remaining on the surface desorb as H₂ between 270 and 400 K, and the CO desorbs between 450 and 550 K. Following a saturation exposure, approximately 0.2 monolayers of methanol decompose to eventually yield CO and H₂ as desorption products. These results are compared to the chemistry of methanol on other metal surfaces.

1. Introduction

The interaction of methanol with metal surfaces is of both fundamental and practical interest for a variety of reasons. For example, the synthesis of methanol from CO and H₂ over transition metal catalysts is an important industrial reaction [1]. Thus, studies of methanol decomposition on well-defined metal surfaces under ultrahigh vacuum (UHV) conditions can serve to isolate and characterize adsorbed CH₃O species that may be of importance in this reaction. From the point of view of the UHV surface scientist, methanol serves as a prototypical example of a weak donor ligand (Lewis base), adsorbing on metal surfaces at sufficiently low temperatures via one or both of the oxygen atom electron lone pairs. However, in contrast to slightly simpler weak donor ligands such as water and ammonia, the presence of the methyl group provides a connection to the surface chemistry of hydrocarbons. Methanol is the simplest molecule that contains C–O, C–H, and O–H bonds, and is thus ideally suited for studies of the relative reactivities of these types of bonds in an adsorbed species.

For all of these reasons, methanol adsorption and decomposition have been studied using a wide variety of experimental techniques on many different single-crystalline transition metal surfaces. These include various low Miller index planes of nickel [2–5], platinum [6], palladium [7,8], ruthenium [9,10], copper [11–14], rhodium [15], tungsten [16], and silver [17]. In this paper, we report the results of a study of the chemistry of methanol on the Rh(100) surface, in which high resolution electron energy loss spectroscopy (HREELS) and thermal desorption mass spectrometry (TDMS) were employed as the primary experimental techniques. This study was undertaken not only to investigate the interaction of methanol with a rhodium surface, but also to provide background for a forthcoming study of the chemistry of methanol on copper overlayers on Rh(100) [18]. The latter issue is currently being pursued as part of an on-going, systematic study of the chemical properties of metal overlayers on metal surfaces [19] and is of particular interest.
given the importance of copper catalysts in both methanol synthesis and the conversion of methanol to formaldehyde [20].

Of particular relevance to this paper are previous UHV studies of methanol adsorption and decomposition on metal surfaces in which the adsorbed intermediates present under various conditions were characterized using HREELS. To date, such studies have been conducted on Ni(111) [2], Pt(111) [6], Cu(100) [11], Ru(001) [9], Pd(100) [7], and Pd(110) [8]. These investigations have revealed many similarities in methanol chemistry on various surfaces, as well as a number of important differences. At liquid nitrogen temperatures, methanol adsorption is generally molecular, although dissociative adsorption to form a chemisorbed methoxy species and hydrogen adatoms occurs on Ru(001) [9] and to some degree on Pd(100) [7]. Annealing the surfaces to higher temperatures results, in all cases, in methoxy formation, usually below 200 K. In some cases, desorption of molecular methanol also occurs as a competing reaction. With further heating, the methoxy species decomposes to adsorbed carbon monoxide and hydrogen. This decomposition occurs near room temperature on most of the surfaces and is often accompanied by a competing reaction, namely the recombinative desorption of methanol from adsorbed methoxy and hydrogen. Interestingly, CH$_3$O and CHO species, which must occur as intermediates in the decomposition of methoxy to CO, have proven very difficult to isolate in these studies; only on Pd(110) has a CHO species formed from methanol decomposition been reported [8]. On Ni(111) [2] and Ru(001) [9], a small amount of CO bond cleavage also occurs during methoxy decomposition.

2. Experimental

2.1. Thermal desorption mass spectrometry (TDMS)

The thermal desorption experiments in this study were performed in a UHV chamber that has been described in detail previously [21]. It is equipped with a double pass cylindrical mirror analyzer with an integral electron gun for Auger electron spectroscopy, LEED optics for low energy electron diffraction observation, and a quadrupole mass spectrometer for thermal desorption measurements. This chamber is pumped by a titanium sublimation pump and an ion pump and the base pressure is in the low 10$^{-10}$ Torr range.

The high purity Rh(100) single crystal was polished using a series of emery papers and diamond paste until a mirror finish was obtained. High purity tantalum wires (0.020” diameter) connected to feedthroughs immersed in a liquid nitrogen reservoir were spot-welded to the periphery of the crystal allowing resistive heating and conductive cooling. A pair of tungsten–5% rhenium/tungsten–26%rhenium thermocouple wires spot-welded to the edge of the crystal was used to monitor the temperature of the crystal.

Spectroscopic grade methanol with a minimum purity of 99.9% was used in this study. Many freeze-pump-thaw cycles were performed prior to introduction of the methanol into the vacuum chamber. Research grade oxygen, hydrogen, and carbon monoxide, supplied by Matheson Gas Products, Inc., were used as received.

The crystal cleaning procedure consisted of oxidation in 1 × 10$^{-7}$ Torr oxygen at 1150 K for 10 min and annealing at this temperature for 5 min. A capillary doser in front of the crystal was used to direct the oxygen and various adsorbates to the crystal surface so that the local pressure near the crystal during oxidation and adsorption was much higher than the background pressure. The amount of methanol dosed on the sample was determined by comparing the 272 eV C(KLL) Auger line with a calibration curve which was measured in a separate experiment by backfilling the chamber with methanol. All exposures quoted are without ionization gauge correction and are given in units of Langmuir (1 L ≡ 1 langmuir = 10$^{-6}$ Torr · s).

A linear heating rate of 10 K/s was used in the thermal desorption experiments.

2.2. High resolution electron energy loss spectroscopy (HREELS)

The HREELS experiments were performed in a two-level UHV system. The upper level contained
an Auger electron spectrometer, LEED optics, a quadrupole mass spectrometer, a sputtering gun, and an ionization gauge. The lower level housed the HREEL spectrometer. The system was pumped using a 220 $\ell$ s$^{-1}$ turbomolecular pump so that the base pressure was typically in the low 10$^{-10}$ Torr range.

The HREEL spectrometer used in these studies was an LK-2000, purchased from Larry Kesmodel Technologies. The resolution (full-width at half maximum of the elastically scattered beam) of the spectra presented and discussed in this paper varies rather widely, from approximately 60–90 cm$^{-1}$. While a resolution of 60 cm$^{-1}$ at an elastic peak count rate of 200,000 cps could typically be obtained from the clean Rh(100) surface, adsorption of methanol resulted in a decreased surface reflectivity which in many cases necessitated the collection of HREEL spectra with less than optimal resolution. The primary energy of the electron beam was typically 2 eV. The spectra presented here were obtained with electron collection in the specular direction, which was approximately 60° with respect to the Rh(100) surface normal. The scan rate for all HREEL spectra except those presented in fig. 8 was approximately 7 cm$^{-1}$ s$^{-1}$.

Crystal cooling, heating, and cleaning were accomplished in manners similar to those described in the TDMS section. In the HREELS chamber, exposures were performed via backfilling the UHV chamber rather than via dosing. Dosing temperatures varied from 125–195 K. All spectra were obtained after flashing briefly to an indicated temperature and recooling; thus only irreversible changes in the HREEL spectra are observed. In addition to experiments conducted with CH$_{3}$OH as discussed in the TDMS section, a few HREELS experiments were performed with CD$_{3}$OD (Aldrich, 99.8 at% D). Exposures of CD$_{3}$OD were never entirely free of H-contamination and the spectra obtained added relatively little to what could be deduced from the CH$_{3}$OH spectra. These CD$_{3}$OD spectra are not shown, but some vibrational frequencies for deuterated species are listed in the tables that follow.

### 3. Results

#### 3.1. Thermal desorption mass spectrometry

Thermal desorption products from methanol adsorbed on the Rh(100) surface at 115 K were CH$_{3}$OH, CO, and H$_{2}$. There was no detectable CO$_{2}$, CH$_{4}$, H$_{2}$O or other products. The signal for mass 31, the strongest fragment in the cracking pattern of CH$_{3}$OH, was used to monitor the desorption of CH$_{3}$OH. Since during the thermal desorption process, the intensity ratio of mass 32/mass 31 stayed constant, we can exclude the possibility that the formation of the mass 31 fragment is a result of the direct desorption of a CH$_{3}$O species.

Fig. 1 shows the mass 31 signal of the thermal desorption spectra of CH$_{3}$OH on the Rh(100) surface following low exposures. At very low coverage, only a single peak ($\beta_2$) appears at 272
K, and shifts to lower temperatures with increasing exposure. A new state ($\beta_1$) appears at 0.76 L around 221 K and shows very little shift with an increase of the exposure. A plot of peak area of $\beta_1 + \beta_2$ versus methanol exposure shows that both of these states saturated following an exposure of $\sim 10$ L. From 1.26 L, a new peak ($\alpha_1$) develops at 153 K. This feature grows with increasing exposure and, as can be seen from fig. 2, does not saturate even above 10 L methanol exposure. The $\alpha_1$ peaks resulting from different exposures exhibit a common leading edge and peak maxima which shift to higher temperature with increasing coverage. This is typical for zero order kinetics and usually indicates the desorption of condensed multilayers. Therefore, this state is assigned to correspond to condensed methanol.

It is shown in fig. 1 that the condensed phase of methanol begins to appear before the chemisorption states are completely saturated. This is likely due to the high sticking probability and low mobility of methanol molecules at the low adsorption temperatures. In the thermal desorption spectrum for a 10.1 L exposure in fig. 2 in which the $\beta_1$ and $\beta_2$ states are both saturated, the peak area of $\alpha_1$ is 1.5 times that of $\beta_1 + \beta_2$.

Solymosi and coworkers have studied the adsorption and decomposition of methanol on Rh(111) and were able to distinguish a physically adsorbed second layer from the multilayers [15]. We were unable to differentiate these two states in our thermal desorption spectra.

In the mass 28 signal of the thermal desorption spectra of methanol on Rh(100), there are small features below 300 K. Their shapes and peak temperatures correspond to those of the mass 31 signal at the same exposures. Therefore, these features are likely due to CO from CH$_2$OH fragmentation. In addition to these small features at low temperature, there is another CO desorption peak above 450 K. Fig. 3 shows this peak at various initial methanol exposures. It can be seen that complete saturation of this state occurs at about 10 L. The peak temperature shifts slightly from 531 K at low coverage to 521 K at saturation coverage, and the peak shape is asymmetric with respect to the peak maxima. This behavior suggests first order kinetics with a coverage dependent activation energy and the desorption of associatively adsorbed CO. The desorption of molecularly adsorbed CO was confirmed by the HREELS results discussed in section 3.2.3. Using the method of Redhead [22] and assuming a pre-exponential factor of $10^{13}$ s$^{-1}$, a binding energy of approximately 130 kJ mol$^{-1}$ is estimated for this CO.

The mass 2 signal of the thermal desorption spectra of methanol on Rh(100), as displayed in fig. 4, shows a large shift in peak temperature from 359 K at low coverage to 326 K at saturation coverage. In addition, the peak shape is symmetric about the maximum temperature. This indicates second order desorption kinetics; i.e., the desorp-
tion of H₂ resulted from the recombination of adsorbed hydrogen adatoms. This state is also completely saturated at about 10 L.

Comparing the CO and H₂ desorption spectra at saturation coverage in this study with those obtained following the separate adsorption of CO and H₂ at saturation coverage on a clean Rh(100) surface gives peak area ratios of 0.37 for CO, and 0.66 for H₂. According to White et al., on the clean Rh(100) surface, saturation coverage for CO is 0.60 ML [23]. Therefore, the CO desorption peak area ratio reveals that approximately 0.22 ML, i.e., $0.31 \times 10^{15}$ methanol molecules/cm², desorbs from the saturated layer in the form of CO. Similar manipulation of the H₂ desorption data assuming a hydrogen adatom saturation coverage of 1.0 [23] gives fairly consistent results; i.e., the amount of decomposing CH₃OH is 0.17 ML. Averaging both estimates leads to the conclusion that approximately 0.2 ML of methanol decomposes following a saturation exposure at low temperature. The CO desorption peak temperatures in this study agree very well with those of thermal desorption spectra of CO adsorbed alone on a clean Rh(100) surface at equivalent coverages [23]. For H₂, the peak maxima in this study are a few degrees lower than those from separate H₂ thermal desorption experiments at equivalent coverages. This is expected, since there are repulsive interactions between H atoms and coadsorbed CO molecules on this surface and thus the H₂ peak desorption temperature can be downshifted by as much as 50 K (depending on CO coverage) when CO is coadsorbed [24].

Fig. 5 shows the dependence of CO desorption on the adsorption temperature of methanol. It is shown that there is no change of the CO desorption spectra when methanol is initially adsorbed onto Rh(100) between 115 and 200 K. From 200
to 300 K, the amount of CO desorbed increases with increasing adsorption temperature and the peak maximum shifts to lower temperature. At 300 K the amount of desorbing CO was a factor of 1.5 larger than after adsorption at 115 K.

3.2. HREELS

The HREELS results obtained in this study indicate that there are three important stages in the adsorption and decomposition of methanol on Rh(100). Below approximately 200 K, methanol is molecularly chemisorbed on this surface. Just above 200 K, changes in the HREEL spectra indicate the formation of a methoxy species via OH bond cleavage of adsorbed methanol. Finally, between approximately 250 and 320 K the methoxy decomposes to form CO and (by inference) hydrogen adatoms. In addition, large methanol exposures below approximately 155 K lead to the condensation of multilayers of methanol on the surface. These various adsorbed phases are discussed separately below.

3.2.1. Molecularly chemisorbed methanol

Exposure of the Rh(100) surface to methanol at temperatures below 200 K led to molecular adsorption of methanol. Fig. 6 shows HREEL spectra that illustrate this. Fig. 6a shows the spectrum that results after a 1 L CH₃OH exposure at 125 K; this exposure corresponds to a coverage that is approximately 1/3 to 1/4 of monolayer saturation. Detailed studies of lower coverages of adsorbed methanol were not feasible due to the weakness of most loss features, and the analysis of higher coverages below 155 K is complicated by the fact that multilayers begin to form before the monolayer is saturated (cf. thermal desorption results). The latter problem could be averted by adsorbing methanol at a surface temperature greater than 155 K. Fig. 6b shows the HREEL spectrum of a saturated monolayer of methanol formed by exposing the Rh(100) surface at 180 K to 30 L of methanol.

Table 1 summarizes the vibrational data of fig. 6a, and gives corresponding data for a low coverage of CD₂OD adsorbed on Rh(100) and for CH₃OH adsorbed molecularly on other metal
Table 1
Vibrational frequencies (cm⁻¹) and mode assignments for chemisorbed methanol on Rh(100), and for CH₃OH chemisorbed on other metal surfaces

<table>
<thead>
<tr>
<th>Mode</th>
<th>CH₃OH</th>
<th>CD₃OD</th>
<th>H/D ratio</th>
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<td>3335</td>
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<td>2960</td>
<td>2205</td>
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<td>δ(CH₃)</td>
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<td>1.33</td>
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<tr>
<td>ρ(δ(CH₃))</td>
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<td>n.r.</td>
<td>—</td>
</tr>
<tr>
<td>υ(CO)</td>
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<td>960</td>
<td>1.05</td>
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<tr>
<td>δ(CH₃)</td>
<td>745</td>
<td>525</td>
<td>1.42</td>
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<tr>
<td>ω(CH₃)</td>
<td>260</td>
<td>265</td>
<td>0.98</td>
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CH₃OH

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<th>Pd(110)</th>
<th>Pt(111)</th>
<th>Ni(111)</th>
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<td>3215</td>
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<td>2975</td>
<td>2930</td>
<td>2955</td>
</tr>
<tr>
<td>2845</td>
<td>2800</td>
<td>n.r.</td>
<td>2810</td>
</tr>
<tr>
<td>1130</td>
<td>1120</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td>1025</td>
<td>1015</td>
<td>1000</td>
<td>1035</td>
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<tr>
<td>770</td>
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<td>700</td>
<td>685</td>
</tr>
<tr>
<td>330</td>
<td>235</td>
<td>n.r.</td>
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</table>

a) Low coverage data of fig. 6a.

b) Low coverage data (1 L at 140 K).

n.r. = not resolved.

surfaces. The mode assignments are straightforward based on the observed frequency shifts upon deuteration, the comparison to other metal surfaces, and comparison to infrared data for gas phase, liquid, and crystalline methanol (cf. section 3.2.4). The presence of the OH stretching and bending modes, the intense CO stretch near 1000 cm⁻¹, and the characteristic CH₃ symmetric deformation mode near 1450 cm⁻¹ combine to indicate that the adsorption is molecular. The fairly intense low frequency mode occurring at 260 cm⁻¹ in (a) is due to the rhodium oxygen stretching vibration; in (b) this mode appears to have downshifted so that it is no longer resolved from the elastic peak. Coordination of the methanol to the surface via the oxygen atom is suggested by the observed frequencies of υ(OH), which are downshifted substantially from the gas phase value of 3681 cm⁻¹. Hydrogen-bonding could also play a role in these lowered frequencies, however. In contrast to υ(OH), the υ(CH₃), δ(CH₃) and ρ(CH₃) vibrational features show relatively small shifts from the corresponding gas phase values, suggesting a largely unperturbed methyl group.

There are some substantial differences between the HREEL spectra of figs. 6a and 6b. Compared to the low coverage of methanol represented in fig. 6a, the higher coverage represented in fig. 6b shows a υ(OH) loss feature that is downshifted approximately 85 cm⁻¹ (from 3335 to 2325 cm⁻¹), and as pointed out above the υ(RhO) feature is resolved in (a) but not in (b). Fig. 6b does show weak loss features at 1770 (π(OH) + υ(CO) combination), 2155 (υ(CO) overtone), and 2580 (υ(CO) + δ(CH₃) combination) cm⁻¹ that are not present in fig. 6a. In addition, the relative mode intensities are different. In fig. 6a, υ(CO) and υ(RhO) are by far the most intense loss features, while in fig. 6b π(OH), δ(CH₃), υ(CH₃), and υ(OH) have all increased markedly in intensity relative to these modes. In fact, the spectrum of fig. 6b closely resembles the multilayer HREEL spectrum of fig. 10, although the signal-to-noise is substantially better for the high coverage monolayer state. The differences between the two spectra of fig. 6 are suggestive of increased interactions among the methanol molecules at the higher coverage and adsorption temperature of spectrum 6b, and will be discussed in more detail in section 4.

3.2.2. Chemisorbed methoxy

It has already been seen that annealing a methanol saturated Rh(100) surface to temperatures slightly in excess of 200 K caused desorption of molecular methanol near 215 K. Corresponding HREELS results show that the methanol that does not desorb in this temperature range undergoes OH bond cleavage to form a chemisorbed methoxy species (and, by inference, hydrogen adatoms [25]).
Fig. 7 illustrates the conversion of chemisorbed methanol on Rh(100) to methoxy. The spectrum of fig. 7a results after a 30 L CH₃OH exposure to the Rh(100) surface at 195 K. The clear presence of the ν(OH) loss feature at 3270 cm⁻¹ indicates that adsorption is still primarily molecular at this temperature, although it is possible that some decomposition to methoxy has already occurred. Upon annealing to 220 K, the spectrum 7b is obtained. This annealing results in a sharpening of the elastic peak (from 88 to 72 cm⁻¹ FWHM) and all observed vibrational modes, and several important spectral changes. Most notably, the ν(OH) loss feature at 3270 cm⁻¹ has disappeared completely, indicating that OH bond cleavage has occurred. The π(OH) (OH out-of-plane bend) loss feature at 725 cm⁻¹ also disappears, leaving only a very weak loss feature at 765 cm⁻¹. This mode could be assigned to a Rh–OCH₃ asymmetric stretching or bending mode [26], to νₕ(RhH) of hydrogen adatoms [25], or to the presence of some residual impurity. The latter interpretation is most likely since this mode is not present in all HREEL spectra of the methoxy species (cf. fig. 9). At the same time, all characteristic vibrations of the methyl group remain. The ν(RhO) mode upshifts to 385 cm⁻¹ and increases in relative intensity, while δₛ(CH₃) and ν(CH₃) decrease in relative intensity. The upshift in ν(RhO) is consistent with a conversion from an oxygen-to-metal lone pair donor bond (adsorbed methanol) to a covalent bond (methoxy). A similar shift of 45 cm⁻¹ was reported for this conversion on the Pd(110) surface.

Thus, the adsorbed methanol simultaneously undergoes two competing channels, either desorption or decomposition to the methoxy species.

Table 2
Vibrational frequencies (cm⁻¹) and mode assignments for chemisorbed methoxy, CH₃O and CD₃O, on Rh(100), and for methoxy (CH₃O) adsorbed on other metal surfaces

<table>
<thead>
<tr>
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<tr>
<td>νₕ(CH₃)</td>
<td>2960</td>
<td>2175</td>
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<td>2910</td>
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<td>2890</td>
<td></td>
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<td>2830</td>
<td>2845</td>
<td>2800</td>
<td>2810</td>
<td>2810</td>
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<tr>
<td>δₛ(CH₃)</td>
<td>1440</td>
<td>1075</td>
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<td>n.r.</td>
<td>1460</td>
<td>1435</td>
<td>1440</td>
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<tr>
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<td>1115</td>
<td>n.r.</td>
<td></td>
<td>n.r.</td>
<td>n.r.</td>
<td>1130</td>
<td>1140</td>
<td>n.r.</td>
</tr>
<tr>
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<td>980</td>
<td>1.03</td>
<td>1010</td>
<td>985</td>
<td>1010</td>
<td>1005</td>
<td>1040</td>
</tr>
<tr>
<td>ν(M–OCH₃)</td>
<td>380</td>
<td>350</td>
<td>1.00</td>
<td>290</td>
<td>380</td>
<td>280</td>
<td>350</td>
<td></td>
</tr>
</tbody>
</table>

a) Shows some frequency shift as a function of annealing temperature.
b) Saturation coverage.
n.r. = not resolved.
The relative intensities of the various loss features of the methoxy species are similar to those of the low coverage adsorbed methanol of fig. 6a and suggest a loss of hydrogen-bonding and/or other molecular interactions compared to the high coverage adsorbed methanol of fig. 7a.

Table 2 summarizes the data of fig. 7b and also gives data for deuterated methoxy on Rh(100) and chemisorbed methoxy on other metal surfaces. Once again, the mode assignments are straightforward and the agreement with the data for other surfaces is excellent. The loss feature at 1810 cm$^{-1}$ in fig. 7b is due to a very small amount of CO adsorbed in bridge-bonded sites. This CO probably originates from adsorption from the chamber background rather than from methoxy decomposition.

Since the disappearance of the (OH) loss feature is the single most crucial piece of evidence in establishing the conversion of methanol to methoxy, separate experiments were also performed in which only the CH/OH stretching portion of the HREEL spectrum was scanned at one quarter of normal speed (i.e., at $\sim$ 2 cm$^{-1}$ per second). Typical results are shown in fig. 8, where fig. 8a corresponds to a low methanol coverage adsorbed at 130 K and 8b–8d to a saturated surface annealed to (b) 214 K, (c) 253 K, and (d) 271 K. The (OH) loss feature is clearly present at 3320 cm$^{-1}$ in (a), while in (b) little if any intensity remains [27]. Note that the resolution of the $\nu$(OH) loss feature in fig. 8a is substantially better than in fig. 6a, which was obtained under virtually identical experimental conditions. For the higher annealing temperatures, the $\nu$(OH) loss feature is completely absent. Thus, these spectra help to confirm the formation of methoxy as discussed above.

3.2.3. Decomposition of methoxy to coadsorbed carbon monoxide and hydrogen

The thermal desorption results of section 3.1 show that, following methanol exposure at low temperature, methanol is desorbed from the Rh(100) surface in the $\beta_2$ peak between approximately 240 and 300 K with apparent second-order desorption kinetics. The preceding HREELS results confirm that this desorption must be due to the recombination of methoxy and hydrogen adatoms, since OH bond cleavage of the adsorbed methanol is complete by 220 K. The HREELS results for higher annealing temperatures indicate that the methoxy that does not desorb as methanol decomposes to CO (and again by inference, additional hydrogen adatoms) between approximately 250 and 320 K. Thus, methoxy undergoes competing desorption and decomposition, similar to the reactions of chemisorbed methanol near 215 K.

Fig. 9 shows the HREEL spectra that result when the Rh(100) surface at 155 K is exposed to 3 L CH$_3$OH (> 75% saturation) and the surface is annealed to (a) 215, (b) 235, (c) 255, (d) 270, (e) 290, (f) 310, and (g) 330 K. In all cases chemisorbed methoxy is present, though virtually all of it has decomposed in (f) and (g), and a very small amount of chemisorbed methanol might still be
Fig. 9. The HREEL spectra that result following a 3 L CH$_3$OH exposure to Rh(100) at 155 K, with subsequent annealing to (a) 215, (b) 235, (c) 255, (d) 270, (e) 290, (f) 310, and (g) 330 K. These spectra illustrate the decomposition of the methoxy species to CO.
present in (a). All spectra also show adsorbed CO, in both bridge-bonded ($\nu$(CO) = 1810–1905 cm$^{-1}$) and on-top ($\nu$(CO) = 1985–2030 cm$^{-1}$) sites. In spectra (a) and (b) only a trivial amount of CO is present, probably due to background adsorption or the decomposition of a small amount of methoxy at defect sites. In (c) the decomposition of substantial amounts of methoxy appears to have just begun, and in (d)–(g) increasingly larger CO loss features appear as the loss features due to methoxy decrease in intensity. Thus, these spectra demonstrate the decomposition of methoxy to CO.

Since very little CO is present in spectra (a)–(c), the surfaces represented by these spectra correspond to virtually pure methoxy overlayers. Two interesting points should be noted. First, the weak loss feature observed in fig. 7b at 765 cm$^{-1}$ is not present in these spectra, supporting the idea that this loss feature is not an intrinsic part of the methoxy vibrational spectrum. Instead, there is a very weak shoulder in (a) and (c) near 650 cm$^{-1}$ which is most likely due to $\nu$(RhH) of adsorbed hydrogen adatoms [25]. Second, there is a continuous upshift of $\nu$(RhO) of methoxy from 355 cm$^{-1}$ in (a) to 405 cm$^{-1}$ in (c), perhaps due to ordering and increased dipole–dipole coupling at higher annealing temperatures. For the higher annealing temperatures of spectra (d)–(g) nothing can be said about the frequency of this mode due to the growing in of the intense $\nu$(RhC) vibration of on-top CO near 470 cm$^{-1}$.

The relative amounts of on-top and bridge-bonded CO produced by background adsorption and/or methoxy decomposition were somewhat variable; this can be seen, for example, by comparing spectrum 7b (no on-top (CO)) to spectra 9a and 9b. However, there was always an increase in the $\nu$(CO) (on-top)/$\nu$(CO) (bridge-bonded) intensity ratio for annealing temperatures above approximately 300 K. This is apparent from a comparison of spectra 9e–9g, and is in accordance with previous vibrational studies of CO adsorbed on Rh(100) [28].

In some cases a third $\nu$(CO) loss feature was resolved near 1750 cm$^{-1}$ as a weak shoulder on the low energy side of the $\nu$(CO) (bridge-bonded) loss feature. This mode is barely visible in figs. 9f and 9g and could be attributed either to CO in a four-fold site [29] or to bridge-bonded CO which is in some way perturbed by the coadsorbates from its ordinary structure. Since this loss feature is sometimes present after annealing as high as 480 K and the thermal desorption spectra show that all H$_2$ has desorbed by 400 K, the interpretation that it might be due to $\nu$(CO) of a CHO or CH$_2$O species is rejected.

Additional HREEL spectra for higher annealing temperatures indicate that the CO formed from methoxy decomposition desorbs below 600 K, consistent with the thermal desorption results.

The decomposition of lower coverages of methanol and methoxy was not studied in as great a detail. The decomposition mechanism at low coverage (i.e., following a 1 L exposure of methanol at low temperature) is the same, although in this case methoxy decomposition is complete by the slightly lower temperature of 295 K.

3.2.4. Methanol multilayers

As has been demonstrated from the thermal desorption results, large exposures of methanol to the Rh(100) surface at temperatures less than 155 K result in the condensation of molecular multilayers of methanol on the surface. The presence of multilayers greatly reduces the surface reflectivity and hence the elastic peak count rate in all multilayer HREEL spectra was $\leq$ 10% of what could be obtained from the clean Rh(100) surface. Nevertheless, these spectra are useful as an additional check of the purity of the methanol being adsorbed on the surface. Fig. 10 shows the HREEL spectrum that results after the Rh(100) surface at 140 K is exposed to 30 L CH$_3$OH. The data of this spectrum are summarized in table 3, along with data for CD$_3$OD multilayers on Rh(100) and with IR data for gas phase [30], liquid [30], and crystalline [30,31] CH$_3$OH. The frequencies of the various vibrational modes of the methanol multilayers on Rh(100) agree most closely with those of crystalline methanol rather than with those of liquid or (especially) gaseous methanol. This is
Fig. 10. The HREEL spectrum that results following exposure of the Rh(100) surface at 140 K to 30 L CH₃OH, showing the characteristic features of multilayer methanol.

particularly true of $\nu$(OH) and $\pi$(OH), but also of $\rho$(CH$_3$) and $\delta$(CH$_3$). This suggests that the multilayers are hydrogen-bonded with a structure similar to crystalline methanol. This is supported by the very broad $\nu$(CH) and $\nu$(OH) loss features. As expected for multilayer vibrational spectra, there is no loss feature in the 250–450 cm$^{-1}$ range that can be attributed to a metal–ligand stretching mode. In addition to the $\pi$(OH), $\nu$(CO), $\rho$(CH$_3$), $\delta$(CH$_3$), $\nu$(CH$_3$), and $\nu$(OH) loss features, fig. 10 exhibits weak features at 1780 and 2530 cm$^{-1}$. These are due to combinations of the loss features observed at lower energy loss: $\pi$(OH) + $\nu$(CO)

$\nu$(OH) = 3245, $\nu$(CH$_3$) = 2980, $\nu$(CH$_3$) = 2855, $\delta$(CH$_3$) = 1475, $\rho$(CH$_3$) = 1180, $\nu$(CO) = 1040, $\pi$(OH) = 765.

Fig. 11. Decomposition mechanism of a saturated methanol layer on Rh(100). Gas phase and adsorbed species are denoted by (g) and (a), respectively.

$(765 + 1040 \sim 1780)$ and $\nu$(CO) + $\delta$(CH$_3$) = (1040 + 1475 \sim 2530).

4. Discussion

The HREELS and thermal desorption results combine to give a consistent overall picture of the reactions of a saturated methanol layer on Rh(100), and this scheme is summarized in fig. 11. Desorption of methanol multilayers occurs near 155 K. The remaining (monolayer) methanol is molecu-

<table>
<thead>
<tr>
<th>Mode</th>
<th>Multilayers on Rh(100)</th>
<th>CH$_3$OH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_3$OH</td>
<td>CD$_3$OD</td>
</tr>
<tr>
<td>$\nu$(OH)</td>
<td>3245</td>
<td>2470</td>
</tr>
<tr>
<td>$\nu$(CH$_3$)</td>
<td>2980</td>
<td>1100</td>
</tr>
<tr>
<td>$\nu$(CH$_3$)</td>
<td>2855</td>
<td>1180</td>
</tr>
<tr>
<td>$\delta$(CH$_3$)</td>
<td>1475</td>
<td>1040</td>
</tr>
<tr>
<td>$\pi$(OH)</td>
<td>765</td>
<td>640</td>
</tr>
</tbody>
</table>

$^a$Not resolved in fig. 10.

n.r. = not resolved.
larly adsorbed up to approximately 200–220 K, where it undergoes competing desorption and decomposition to a methoxy species. The methoxy is stable to approximately 250 K; between 250 and 320 K it either recombines with hydrogen adatoms to desorb as methanol or decomposes to carbon monoxide and additional hydrogen adatoms. Recombinative desorption of H₂ occurs between 270 and 400 K, and the desorption of molecular CO occurs between 450 and 550 K, regenerating the clean Rh(100) surface. Following a saturation methanol exposure, approximately 0.2 monolayers of methanol decompose eventually to CO and hydrogen.

This decomposition mechanism is similar to those that have been reported for methanol decomposition on other metal surfaces, particularly Ni(111) [2], where conversion of methanol to methoxy occurs near 180 K and the methoxy decomposes to CO by about 300 K. On Ru (001), methoxy formed from methanol decomposition decomposes between 220 and 300 K, but, in this case, methanol adsorbs dissociatively as methoxy + H(ads) even at 85 K [9]. On Pd(100), adsorption is partly dissociative (to methoxy and H(ads)) and partly molecular at 77 K, while decomposition of the methoxy to CO is complete by approximately 300 K [7]. On Pd(110) methanol adsorbed at 110 K converts to methoxy by 200 K and the methoxy decomposes below 300 K [8]. Thus on clean metal surfaces where methanol decomposition has been monitored using HREELS, the temperature range in which methoxy decomposes appears to be fairly constant, independent of both the nature of the metal and the surface structure. However, the temperature at which adsorbed methanol undergoes OH bond cleavage to form methoxy appears to vary widely, although it is similar for Rh(100), Ni(111), and Pd(110). The large reported variations in this temperature do not appear to show a strong correlation with either metal type or surface structure.

As on most other metal surfaces where methanol decomposition has been characterized with HREELS, no CH₂O or CHO intermediate in the decomposition of methoxy to CO could be identified on Rh(100). The one exception to this trend appears to be the Pd(110) surface [8], where after annealing a saturated methanol layer to 300 K, weak loss features were observed near 1550 and 1650 cm⁻¹ that were tentatively attributed to one or more adsorbed CHO species. Since on a sufficiently small time scale both CH₂O and CHO must be present when methoxy decomposes to CO, this trend indicates that these intermediates are almost always less stable than adsorbed methoxy at the temperature (~300 K) where this decomposition occurs. From a kinetic viewpoint, the reactions

\[ \text{CH}_2\text{O (ads)} \rightarrow \text{CHO (ads)} + \text{H (ads)}, \quad (i) \]

and

\[ \text{CHO (ads)} \rightarrow \text{CO (ads)} + \text{H (ads)}, \quad (ii) \]

must have lower activation barriers than the reaction

\[ \text{CH}_2\text{O (ads)} \rightarrow \text{CH}_2\text{O (ads)} + \text{H (ads)} \quad (iii) \]

(the (ads) denotes an adsorbed species). Thus reactions (i) and (ii) follow immediately upon the occurrence of reaction (iii), and one observes spectroscopically only the net reaction CH₂O (ads) → CO (ads) + 3H (ads).

As table 1 shows, the chemisorbed methanol formed on Rh(100) is similar to chemisorbed methanol formed on other metal surfaces. In all cases methanol is believed to be adsorbed to the metal surface via the oxygen atom, with one or both oxygen atom lone pairs forming donor bonds to the surface. This interaction can be thought of in classic Lewis acid–Lewis base terms, with methanol acting as the Lewis base and the metal surface as the Lewis acid. This bonding mechanism is supported on several surfaces [3,7,32] by work function measurements, which show that the work function decreases monotonically as methanol is adsorbed. The HREELS results also support this bonding mode, since on all surfaces where chemisorbed methanol has been vibrationally characterized, ν(OH) is downshifted > 300 cm⁻¹ from the gas phase value of 3681 cm⁻¹. At the same time the frequencies of the various methyl vibrations are virtually unchanged (with the possible exception of the methyl rock, which upshifts 60–70 cm⁻¹). Bonding via the oxygen atom is of course expected for the methanol molecule;
without cleaving any CH bonds, there is no way (apart from van der Waals interactions) for adsorption to occur via the saturated carbon atom.

The results presented in this paper do not allow firm conclusions to be drawn about the symmetry or adsorption site of the chemisorbed methanol on Rh(100). However, the similarities in the vibrational spectra of adsorbed methanol on a number of surfaces of different structure suggest a common adsorption site, and such a site could only be an on-top site or two-fold bridging site since sites of higher symmetry are not available on all of the surfaces. In addition, since the methanol oxygen atom has two lone pairs, a coordination number higher than two is not expected; and approximately tetrahedral geometry for the oxygen atom can be obtained only for adsorption in an on-top or two-fold bridging site. We tentatively favor the bridge-bonded site which should allow a stronger interaction with the surface and which has been tentatively favored as the site where methanol undergoes OH bond cleavage on Ru(001) [9], but further investigation of this point is clearly needed.

The adsorbed methanol could be of either C₃ or C₄ symmetry. The observation of the ν(CH₃) and νₗ(CH₃) modes in specular HREEL spectra supports C₃ symmetry, but these modes are too weak to allow detailed angular profiles of their intensities to be obtained.

As pointed out in section 3.2.1, HREEL spectra of low and high coverages of adsorbed methanol on Rh(100) show a number of differences which can be attributed to increased adsorbate-adsorbate interactions at higher coverages. In terms of relative mode intensities, spectra of low coverages of methanol resemble closely those of methoxy, with ν(Rh-O) and ν(CO) dominating the spectra, while spectra of high coverages of methanol show much more intense ν(OH), δ₁(CH₃), ν(CH₃), and ν(OH) modes, similar to the spectra of methanol multilayers. These changes suggest that the interactions present for high coverages, probably including substantial hydrogen-bonding, result in reorientation of at least some of the adsorbed methanol such that increased dynamic dipoles perpendicular to the surface become associated with some of the hydrogenic vibrational features. The decrease in frequency of ν(OH) as the coverage increases also suggests that increased hydrogen-bonding occurs at high coverages. If there were no hydrogen-bonding, the ν(OH) frequency should increase with increasing coverage, as the oxygen-to-metal charge transfer per molecule becomes less at higher coverages.

Table 2 shows that the methoxy formed on Rh(100) is vibrationally very similar to methoxy species formed on other metal surfaces; this is true not only with regards to mode frequencies but also relative mode intensities. The loss features due to ν(Rh-O) and ν(CO) are by far the most intense for all coverages and annealing temperatures. Off-specular HREEL spectra (not shown) show that both of these loss features are attenuated relative to the various hydrogenic modes, indicating that these two modes are excited primarily via the dipole scattering mechanism while the hydrogenic modes scatter primarily via non-dipolar mechanisms. The intensity of ν(CO) suggests strongly that (as expected) the methoxy CO bond is not parallel to the surface, but the exact RhOC bond angle cannot be deduced from these data. Studies of methoxy on other surfaces have come to differing conclusions regarding adsorption site and CO bond orientation. On Ni(111) [2] and Pd(100) [7], the observation of νₗ(CH₃) in specular HREEL spectra has been taken as evidence for a tilted methoxy species; i.e., the methoxy CO band is not normal to the surface plane. An X-ray photoelectron diffraction study of methoxy on Cu(110) [12] also supported a tilted methoxy species on this surface. In contrast, an IRAS study of methoxy on Cu(111) led to the conclusion that the methoxy species was upright (i.e., the CO bond is perpendicular to the surface), occupying a 3-fold hollow site and with C₃ᵥ symmetry [13]. A NEXAFS study of methoxy on Cu(100) also concluded that methoxy stands upright on that surface [14]. The observation of νₗ(CH₃) and ρ(CH₃) in specular HREEL spectra of methoxy on Rh(100) could also be taken as evidence for a tilted rather than an upright methoxy; for a tilted methoxy of C₃ symmetry these modes would be “dipole allowed” (though the dynamic dipoles associated with them should be weak). Interestingly, the authors of the IRAS study on Cu(111) [13] point out that while
tilted, 2-fold bridge-bonded methoxy ligands are known in organometallic compounds such as Os₅(CO)₁₀ (μ-H) (μ-OCH₃) [33], upright methoxy species in higher coordination sites are apparently unknown in organometallic chemistry. Based on the analogy to organometallic compounds, we favor a tilted, 2-fold bridging methoxy on Rh(100). However, this preference is speculative, and it seems clear that additional studies employing a variety of experimental techniques are needed to establish general trends about the bonding and structure of methoxy on metal surfaces.

An additional point of interest concerning methoxy on Rh(100) is the fact that ρ(RhO) up-shifts with increasing annealing temperature, from 355 cm⁻¹ in fig. 9a to at least 405 cm⁻¹ in fig. 9c. An upward shift of 50 cm⁻¹ in the frequency of this mode (from 320 to 370 cm⁻¹) with increasing annealing temperature was also observed on Ru(001) and was tentatively identified with a change in adsorption site [9]. Since none of the other vibrational loss features of methoxy show consistent shifts as a function of annealing temperature on Rh(100), we do not favor this interpretation. It seems more likely that this frequency shift results from increased dipole–dipole coupling as the methoxy layer becomes more ordered at higher annealing temperatures.

5. Conclusions

The principal conclusions of this work are the following:

(1) Below approximately 200 K, methanol adsorbs molecularly on the Rh(100) surface. The molecule bonds to the surface via one or both of the oxygen atom electron lone pairs, in a Lewis acid-base interaction. There are some changes in the vibrational spectrum of the adsorbed methanol as the (submonolayer) coverage is changed, suggestive of hydrogen-bonding of methanol molecules within the monolayer.

(2) Near 210–220 K, part of the adsorbed methanol desorbs and the rest undergoes OH bond cleavage to form an O-bonded methoxy species. The methoxy species is stable to approximately 250 K, and its vibrational spectrum is very similar to those of methoxy species that have been vibrationally characterized on other metal surfaces.

(3) Between 250 and 320 K, the methoxy either recombines with adsorbed hydrogen adatoms and desorbs as methanol, or decomposes to form coadsorbed carbon monoxide and hydrogen adatoms. As in the case of CO adsorption on clean Rh(100), the CO formed occupies both bridging and on-top adsorption sites, and the relative populations of CO in these two binding sites are temperature dependent. As in the case of methanol decomposition on most other metal surfaces, no intermediate in the decomposition of methoxy to CO could be identified using HREELS. There is no evidence for carbon–oxygen bond cleavage of the methoxy species.

(4) The hydrogen adatoms recombine and desorb as H₂ between approximately 270 and 400 K. This is reduced from the H₂ desorption temperature range from clean Rh(100) due to the presence of coadsorbed CO. The CO desorbs near 500 K, regenerating the clean Rh(100) surface.

(5) Molecular multilayers of methanol can be condensed on Rh(100) at temperatures below approximately 150 K. The vibrational spectra of these multilayers are very similar to spectra of crystalline methanol.

(6) Following a saturation methanol exposure to Rh(100) at approximately 115 K, annealing the surface leads eventually to the decomposition of ~ 0.2 monolayers of methanol to yield ultimately CO and H₂ as desorption products. Since some methanol also desorbs molecularly, the saturation coverage in the first monolayer is somewhat higher than this.

Acknowledgements

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References

[25] At a saturation coverage of hydrogen, the symmetric metal-hydrogen stretch occurs near 660 cm⁻¹ on this surface, but the intensity of this loss feature is low.
[27] A mode of similar intensity was observed in the HREEL spectrum of methoxy on Ru(001) at 615 cm⁻¹, and was tentatively assigned to a Ru–OH₂ mode of a small amount of adsorbed water or to a Ru–OCH₃ asymmetric stretching or bending mode of methoxy [10].
[28] It must be pointed out that after annealing the surface to > 200 K and recooling to <150 K, the readsorption of a small amount of methanol or water from the chamber background could lead to a very weak ν(OH) loss feature in the subsequently collected HREEL spectrum. We thus believe that cleavage of the OH bond of the initially adsorbed methanol is virtually complete in fig. 8b.