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Adsorption of Methyl Radicals on the Oxygen-Modified Mo(100) Surface

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Abstract: The adsorption and surface reactions of free gas phase methyl radicals on oxygen-modified Mo(100) have been studied using a combination of temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). Methyl radicals were found to adsorb on the surface at room temperature. Upon heating the surface methyl groups decompose to form surface hydrogen. The surface hydrogen hydrogenates the remaining intact methyl groups leading to methane which desorbs from the surface. The carbon produced by dehydrogenation combines with surface oxygen to yield CO. Comparison of the surface chemistry and the measured C(1s) binding energy with surface methoxy and with CH_3 bonded to metal surfaces indicates that the methyl groups are primarily bonded to surface metal atoms to form a metal alkyl rather than to surface oxygen.

1. Introduction

Chemical reactions which involve free radicals as intermediates are one of the major classes in chemistry. Hydrocarbon free radicals are proposed intermediates in combustion, polymerization, lubricant degradation, and metal organic chemical vapor deposition of thin films. All of these reactions occur in the presence of solid surfaces that may play an important role in the formation, destruction, and propagation of the radicals. In spite of this situation little is understood about the interactions between radicals and surfaces. To quote a 1985 monograph on the subject of combustion: "The precise role of the heterogeneous [radical] reactions is unknown because, in most cases, they have been, unjustifiably, completely ignored. The evidence for their involvement is, however, overwhelming and is based on a variety of observations."

The present paper reports on a study of gas phase, free methyl radicals interacting with a single crystal surface in ultra-high-vacuum. Temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) were employed to study the adsorption and surface chemistry of methyl radicals on single-crystal Mo(100) surfaces modified by controlled coverages of atomic oxygen (hereafter referred to as O/Mo(100)). The geometric and electronic structure of these surfaces have been characterized extensively as have their surface chemistry.[2] The gas phase methyl radicals were produced by low-pressure thermal decomposition of azomethane flowing through a hot alumina or quartz tube. Careful measurements have been performed to establish the identity and partial pressure of the methyl radicals as well as the various side products (nitrogen, hydrogen, methane, ethane, and chloromethane) produced by the methyl radical source. The radicals were allowed to impinge on the oxygen-modified Mo(100) surface under conditions where it was established that none of the side products of azomethane decomposition adsorb on the surface. The nature of the adsorbed species and surface reaction pathways were studied using XPS and TPD and will be reported here. In an effort to understand the surface chemistry of adsorbed methyl and to check for interference from the side products of azomethane pyrolysis, the chemisorption and surface chemistry of hydrogen, nitrogen, methane, ethane, azomethane, methanol, and chloromethane were also studied. A description of the methyl radical source, its characterization, and a brief report of experimental results on the interaction of methyl radicals with O/Mo(100) have appeared elsewhere.[3,4]

Table I. Gas Composition Produced by the Azomethane Pyrolysis (mole fractions)

N_2	0.18	CH_3	0.14	H_2	0.02
Ar	0.47	CH_4	0.13	CH_3NNCH_3	0.004
		C_2H_6	0.05		

2. Experimental Section

Most of the experiments were conducted in an ultra-high-vacuum (UHV), surface science apparatus which has been described previously (see Figure 1).[3,5] Briefly, the turbomolecular and diffusion pumped UHV chamber (operating pressure 2×10^{-10} Torr) contains facilities for XPS, TPD, sample cleaning via inert gas ion sputtering, introduction of gases, and methyl radical dosing. XPS was performed using an unfiltered Al Kα X-ray source (1486.6 eV) and a hemispherical electrostatic analyzer (AEI ES200) operating at a constant retard ratio of 20. XPS peak positions are reported as binding energies (BE) referenced to the metallic Mo($3d_{5/2}$) level at 227.7 eV. TPD was monitored with a quadrupole mass spectrometer (VG SX-200) interfaced to an IBM compatible microcomputer. The mass spectrometer was housed in a separate chamber pumped by an 11 L/s ion pump and a pumping by-pass line that connects to the main chamber just above the turbo pump and 17 cm below the sample. Desorption flux is spatially filtered by a 3-mm aperture $\sim$20 mm from the sample to minimize signal from the sides and back of the sample. Additional XPS measurements of adsorbed methyl were performed in a VG Scientific ESCALAB/SIMSLAB ultra-high-vacuum instrument using a Mg Kα X-ray source.

The sample was mounted on a heatable/coolable sample probe. The probe permits translation along and rotation about an axis in the plane of the sample. The sample was held by spot welding to two 0.25 mm tantalum wires which in turn were spot welded to two 3 mm OD nickel tubes. The nickel tubes in combination with a cryogenic electrical isolator provide the means to circulate liquids or gases for cooling the sample and to make electrical connection to the sample for resistive heating. With this arrangement the sample could be heated to 1275 K or cooled to 100 K by passing liquid nitrogen through the nickel tubes. Temperatures were measured by a chromel–alumel thermocouple spot welded to the sample.

The methyl radical source design and characterization has been described in ref 3. Briefly, gas phase methyl radicals were formed by low-pressure pyrolysis of azomethane (*trans*-dimethyldiazene), CH_3NNCH_3, in a heated alumina tube directed toward the sample at 45° to the normal (see Figure 1). The end of the methyl radical source tube was approximately 2.5 cm from the sample. Azomethane was synthesized according to the procedure of Renaud and Leitch[6] and purified by vacuum distillation and freeze–pump–thaw cycles. The azomethane was stored in a stainless steel reservoir and admitted into the alumina tube through a standard leak valve. The particular source employed for the studies reported here achieved a pyrolysis conversion of 98%. 100%

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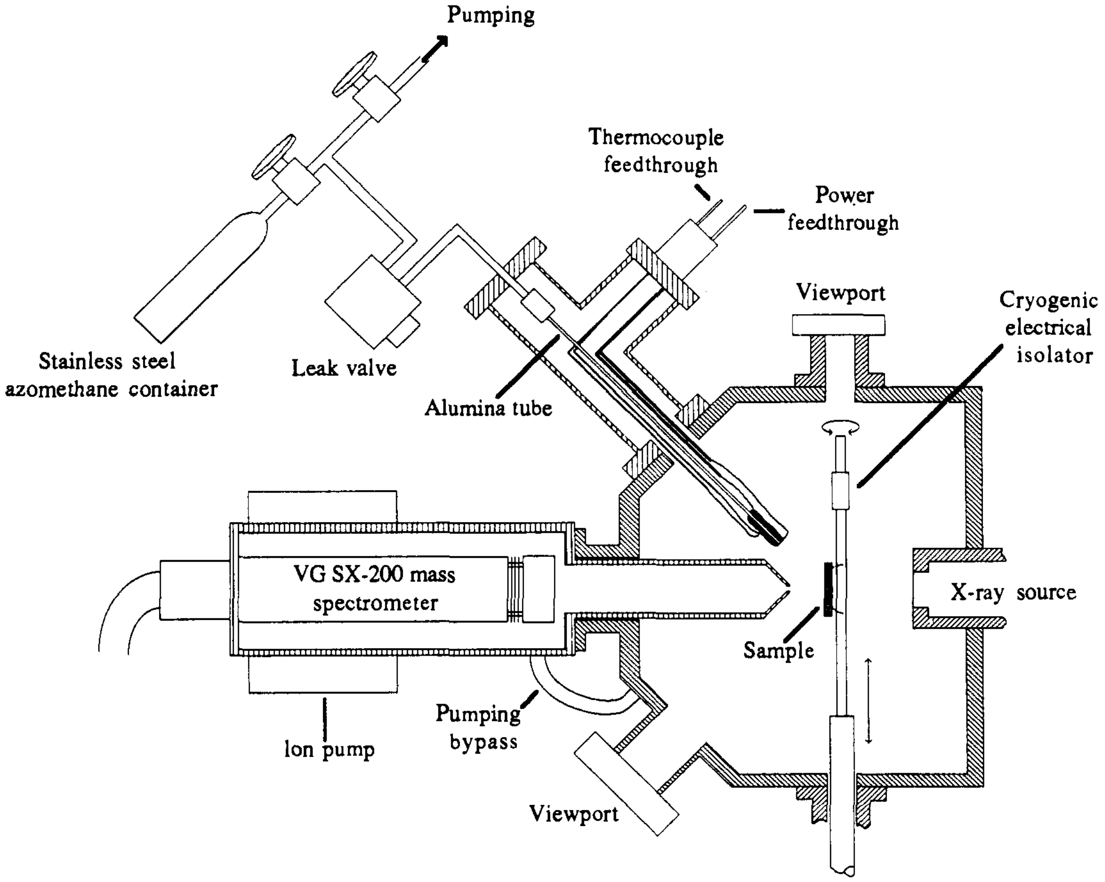

Figure 1. Schematic diagram of the surface science apparatus employed for the experiments.

conversion has been achieved subsequent to this work.[4] The gas composition produced by the source, listed in Table I, was determined by careful analysis in a separate vacuum chamber using line-of-sight, quantitative mass spectrometry and appearance potential measurements.[3]

The sample was a 1-cm-diameter Mo(100) single-crystal disk that was cut and mechanically polished to within 1° of the 100 plane. It was initially cleaned in a separate UHV chamber by heating to 1500 K in 5×10^{-7} Torr of oxygen for 48 h to remove bulk carbon and sulfur. Routine cleaning of the crystal was performed by exposing the sample at 1023–1173 K to 20–30 L (1 L = 10^{-6} Torr·s) of O_2 to remove surface carbon followed by argon ion sputtering to remove the oxygen and annealing at greater than 1173 K to order the surface. A Mo(100) surface covered by 1 monolayer (ML) of atomic oxygen was prepared by exposing the clean surface at room temperature to 2.3 L of oxygen followed by annealing at $\geq$1173 K. Higher oxygen coverages were prepared by exposure to O_2 at a sample temperature $\geq$1023 K. MoO_2 was formed at 873 K by an O_2 exposure of 30000 L.

All gases were admitted using the alumina pyrolysis tube. $^{\bullet}CH_3$ exposures were conducted with the sample near room temperature. TPD experiments were performed with temperature ramps between 10 and 15 K/s. During TPD experiments, the ion pump on the mass spectrometer chamber was turned off. Fifteen masses along with the temperature can be followed at one time. However, the sampling rate decreased with each additional mass followed. Typically, less than 10 masses were followed. Adsorbate coverages were determined by comparison of the time integrated desorption peak areas with the peak area measured from the saturated β-CO state which corresponds to 0.5 ML of dissociated CO.[7] The time integrated pressure for the molecule, P(M), is given by

$$P(\mathrm{M}) = (1/\chi_\mathrm{M})\sum_\mathrm{m} I_m(M)/T_m g_m \qquad \mathrm{(E1)}$$

where I_m(M) is the measured time integrated mass current of a particular mass fragment, m, from molecule, M; χ_M is the ionization cross section taken from Harris et al.;[8] T_m is the mass-dependent transmission supplied by the manufacturer of the mass spectrometer; and g_m is the mass-dependent electron multiplier gain. The summation includes all fragment ions and the parent ion. T_m and g_m are approximately constant for the fragment ions from the molecules observed in this study (H_2, CH_4, CO). With this assumption the time integrated pressure can be written in terms of a single time integrated ion signal:

$$P(\mathrm{M}) = I_\mathrm{m}/\chi_\mathrm{M} T_\mathrm{m} g_\mathrm{m} A_\mathrm{m} \qquad \mathrm{(E2)}$$

where A_m(M) is the ratio of the peak height for the mass fragment at the measured mass divided by the sum of all mass fragment peak heights for the molecule of interest, $A_\mathrm{m}(\mathrm{M}) = I_\mathrm{m}(M)/\sum_{\mathrm{m}'} I_{\mathrm{m}'}(\mathrm{M})$. The coverage in monolayers was found by dividing this total pressure by twice the time integrated pressure from the saturated β-CO state. Since the apertured mass spectrometer collects only a restricted solid angle above the surface, this procedure depends on the assumption that all desorbed molecules have similar desorption angular distributions.

$^{\bullet}CH_3$ exposures were determined from the measured gas composition entering the UHV chamber (see Table 1), the pressure rise during exposure measured by the ion gauge, and a correction to the measured pressure rise which accounts for the dosing geometry. This correction was obtained from the apparent sticking coefficient for CO on clean Mo(100) measured in our apparatus using TPD and XPS data to determine coverage and the ion gauge to determine apparent exposures. Since the literature value of the CO sticking coefficient on clean Mo(100) is 0.3[9] and the apparent value was 9, the pressure at the sample due to the dosing geometry is approximately 30 times the pressure measured at the ion gauge. Exposures determined in this way will be in error (1) due to preferential loss of $^{\bullet}CH_3$ from the gas phase (by adsorption) between the pyrolysis source and the ion gauge and (2) because no correction has been made for the ion gauge sensitivity to the gas composition produced by the pyrolysis source. The first error will be no more than 14% since that is the fraction of $^{\bullet}CH_3$ in the dosing gas. The second error will be small since the ion gauge has been calibrated for nitrogen, the calibration factor for argon is approximately the same, and these gases make up the majority of the dosing gas.

3. Results

1. Methyl Radical. Following exposure of O/Mo(100) surfaces to pyrolyzed azomethane, methane (16 amu), hydrogen (2 amu), and CO (28 amu) were the major species detected by TPD. Representative TPD spectra from a saturation coverage of $^{\bullet}CH_3$

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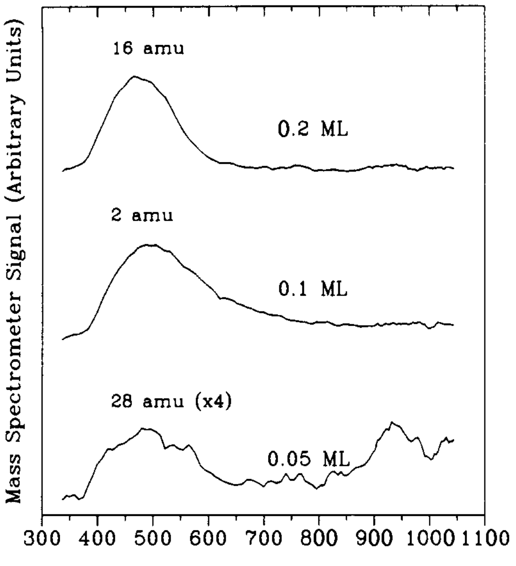

Figure 2. Temperature programmed desorption of methane (16 amu), hydrogen (2 amu), and carbon monoxide (28 amu) following adsorption of methyl radicals on the 1.0 ML O/Mo(100) surface.

on 1 ML of O/Mo(100) are shown in Figure 2. Methane gave rise to a single desorption peak centered at 450 K. The hydrogen desorption peak was centered at 500 K. CO was produced in two peaks centered at 480 and 950 K. The high-temperature peak corresponds to the β-CO reported previously[7] and is due to reaction of the adsorbed oxygen with atomic carbon produced by dissociative adsorption of CH_3 at bare metal sites on the surface (see Discussion). At oxygen coverages >1 ML, where no bare metal sites remain, no β-CO was detectable. The α-CO peak is due partly to adsorption of CO from the background but mainly to decomposition of CH_3 followed by reaction of the resulting carbon with surface oxygen as discussed below. The onset of desorption for all three molecules was 375 K. The approximate coverages were 0.2, 0.09, and 0.05 monolayer for CH_4, H_2, and CO, respectively. Trace amounts of ethane (<1% of the methane product) were detected in some experiments. Methanol, formaldehyde, and ethylene were looked for but were not detectable. No nitrogen-containing molecules such as N_2, ammonia, or methylamine were detected. XPS measurements following TPD showed that no carbon remained on surfaces with oxygen coverages ≥1 ML.

Table II. Yield of Methane and Hydrogen from Different Dose and TPD Orientations

$^{\bullet}CH_3$ exposure (L)	dose orientation (deg)	TPD orientation (deg)	CH_4 yield (ML × 10^{-3})	H_2 yield (ML × 10^{-3})
0	0	0	0.5	*a*
0.21	0	0	7.5	*a*
0.21	0	0	6.1	*a*
0.21	0	180	1.4	*a*
0.21	90	0	1.7	*a*
0.21	0	0	6.5	*a*
0	0	0	1.2	*a*
0.21	180	180	2.3	*a*
0.21	180	180	1.6	*a*
0.21	0	180	1.3	0.6
0.21	0	0	5.5	1.6
140	0	0	170	82
140	0	180	130	137

[a] Not measured.

Figure 3a shows the CH_4 (16 amu) TPD spectra obtained from a 1.0 ML O/Mo(100) surface with various $^{\bullet}CH_3$ coverages. The spectra are depicted as the measured points with a smooth curve superimposed. These data are representative of all the oxygen

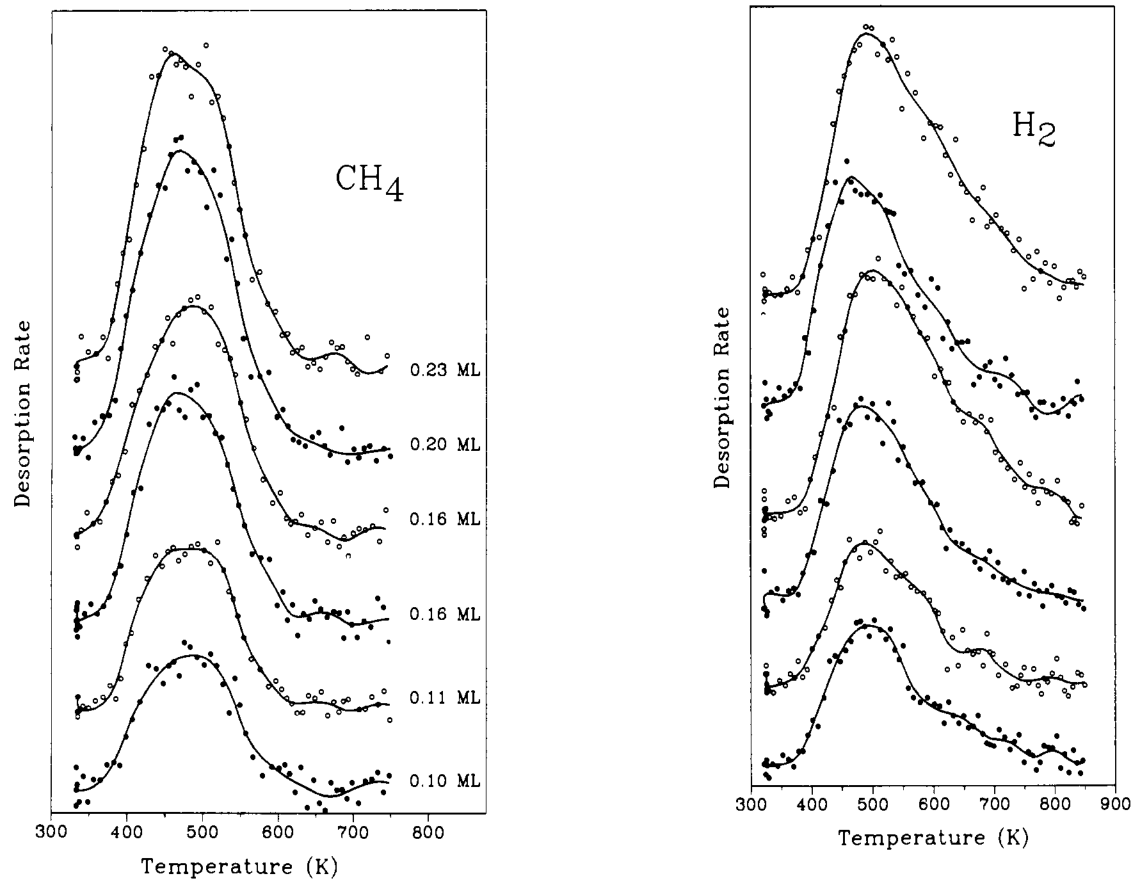

Figure 3. Temperature programmed desorption of methane (a, left) and hydrogen (b, right) from various coverages of methyl adsorbed on a 1.0 ML O/Mo(100) surface.

precoverages studied. The peak is broader than usually seen for desorption from single-crystal metal surfaces (110 K fwhm), but the width is typical for oxygen-modified Mo(100) surfaces (see for example ref 10). The peak temperature is approximately independent of methyl exposure and coverage consistent with overall first-order kinetics for the surface reaction leading to methane desorption (see discussion). Methyl exposures ranging from 4 to 700 L were employed in random order to establish that 125 L was sufficient to saturate the yield of methane from the surface. This exposure was also sufficient to achieve saturation yields of methane on other O/Mo(100) surfaces with oxygen coverages near 1 ML although the amount of methane corresponding to the saturation yield did depend upon oxygen precoverage. Figure 4 shows the saturation methane yield obtained for various oxygen precoverages and for MoO_2. The maximum yield occurs for an oxygen coverage of approximately 1 ML and decreases with increasing oxygen coverage above 1 ML. A lower methane yield was also observed from the O/Mo(100) surface with 0.25 ML of oxygen coverage due to dissociative adsorption on bare metal patches (see XPS data below) as has been observed previously with other hydrocarbons.[10] Surface atomic carbon produced by dissociation desorbs as CO.

H_2 TPD spectra corresponding to the methane results are shown in Figure 3b. The H_2 desorption peak is very broad, and there is also a significant shoulder on the high-temperature side. Unlike the methane peak the H_2 peak area did not saturate with increasing methyl radical exposure. These observations suggest the possibility that the side or back of the sample or the mounting hardware that is heated with the sample may contribute to the measured H_2 desorption signal. To clarify which surfaces were responsible for the observed products, the sample was rotated to different orientations for exposure and desorption. The results from various combinations of orientations are presented in Table II with the low exposures (0.21 L) presented in the order in which the experiments were performed. Zero degrees is defined as the orientation where the sample normal pointed toward the mass spectrometer and 45° to the $^\bullet CH_3$ source. 180° corresponds to the surface facing away from the doser and the mass spectrometer. 90° corresponds to the sample face oriented at 90° from the mass spectrometer and toward the turbomolecular pump. The time between runs was about 5 min. The higher exposures were performed after several previous large $^\bullet CH_3$ doses. Clearly the highest yields of methane were measured when the front surface faced the $^\bullet CH_3$ source during dosing and the mass spectrometer during TPD. With the exception of the first dose, the diffuse CH_4 yield from the 0.21 L exposures was nearly constant at less than 25% of the intensity obtained when adsorption and desorption took place on the front face of the crystal. These two results indicate that methane signals came primarily from the front surface of the Mo(100) crystal. In contrast the yield of hydrogen at high exposure was larger from the back of the sample than from the front. Thus desorption from the sample support wires and other surfaces in the vicinity of the sample was a significant fraction of the measured H_2 TPD signal. As a consequence of this result a hydrogen mass balance cannot be computed nor can the yields of hydrogen and methane be compared quantitatively.

The α-CO peak shown in Figure 2 was observed over the same temperature range as the methane peak in all desorption experiments. The CO peak area was an approximately constant fraction of the CH_4 peak area. The coverage corresponding to this peak averaged 29 ± 6% of the coverage corresponding to the methane peak. The scatter in this percentage was due in part to adsorption of CO from the background and in part to noise in the small CO TPD peak.

Figure 5 depicts the C(1s) XPS spectrum following saturation methyl radical exposure to a 0.7 ML O/Mo(100) surface. The data are presented as the difference in measured spectra before and after methyl radical exposure in order to remove the sloping background characteristic of the XPS spectra in this energy region measured from O/Mo surfaces. The narrow peak at 282.6 eV is an indication of carbidic carbon on the surface. Carbidic carbon due to decomposition on bare metal patches is typically observed following hydrocarbon exposure to O/Mo(100) with oxygen coverages less than 1 ML. This peak grows in first as a function of methyl exposure followed by a broader peak (2.0 eV fwhm) centered at 284.6 eV. The width of the latter band suggests the presence of multiple surface species or a single species in multiple adsorptions sites. The total area of the XPS carbon signal corresponds to ~0.5 ML.

2. Azomethane, Methane, Ethane, Nitrogen, Hydrogen, Deuterium, and Chloromethane Adsorption. Adsorption of azomethane was studied to determine what, if any, contribution to the results obtained following $^\bullet CH_3$ can be attributed to the residual 2% azomethane remaining from pyrolysis. Small hydrogen and carbon monoxide desorption peaks were detectable after very large azomethane exposures (100 times the equivalent exposure during methyl radical dosing). No methane desorption was detectable. No detectable N(1s) XPS peak was observed after azomethane exposure at room temperature. A small carbon peak was detectable at about 285.5 eV.

Generation of methyl radicals by decomposition of a stable precursor molecule always entails formation of side products. When selecting an appropriate precursor to methyl radicals, a decomposition procedure, and a solid surface for study, one criterion which had to be met in order to avoid ambiguity in data interpretation was that adsorption of the precursor or of the side products should not interfer with methyl radical adsorption. The low-pressure pyrolysis of azomethane produces a number of side products in addition to the desired methyl radicals. These include methane, ethane, nitrogen, hydrogen, unreacted azomethane, and possibly a trace (undetectable) of chloromethane (see Table I).

TPD experiments were performed for adsorbed methane, ethane, nitrogen, hydrogen, and deuterium following exposure to the sample at ~100 K with the gases at room temperature. H_2 and CH_4 were also dosed through the alumina tube heated to 1273 K, but no differences from room temperature gases were detectable in the TPD. In particular there was no evidence for adsorption of atomic hydrogen that might be generated by dissociation of H_2 on the heater. All of these molecules desorbed in a single, low-temperature desorption peak. These peaks were at 135, 164, 148, 134, and 135 K for CH_4, C_2H_6, N_2, H_2, and D_2, respectively.

Chloromethane (CH_3Cl) is also a possible trace impurity in azomethane.[11] TPD spectra showed that desorption was complete by 300 K. Cl(2p) XPS recorded following adsorption at 170 K revealed that all chlorine had left the surface after heating to 276 K.

3. Methanol. One possible surface species that may form as a result of $^\bullet CH_3$ adsorption on O/Mo(100) is surface methoxy, OCH_3. It is known from HREELS studies that surface methoxy forms on clean and partially oxidized Mo(100) surfaces as a result of methanol adsorption at and below room temperature.[12,13] TPD results from adsorption of CH_3OH on a 1 ML O/Mo(100) surface at 100 K were essentially identical to those of Miles et al. (see ref 13, Figure 6). No methane was detectable in our experiments and none was reported by Miles. TPD spectra were also recorded following adsorption of CH_3OH on a surface with submonolayer oxygen coverage (0.4 ML) at 200 K. A small methane peak corresponding to less than 5% of the adsorbed methanol was observed. The hydrogen and CO desorption data reproduce the results reported by Miles et al.[13] and Ko and Madix[14] following methanol adsorption on a clean Mo(100) surface. The evolution of methyl radicals, as reported by Serafin and Friend[15] on the oxygen-modified Mo(110) surface following methanol exposure, was never detected on any O/Mo(100) surface. The C(1s) XPS spectrum from CH_3OH adsorbed at room temperature on a

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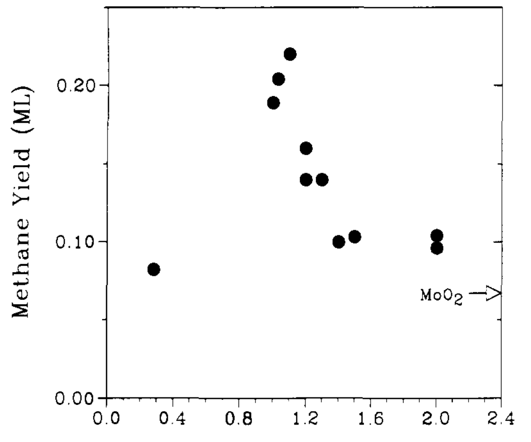

Figure 4. Saturation methane yield from surfaces with various precoverages of oxygen on Mo(100).

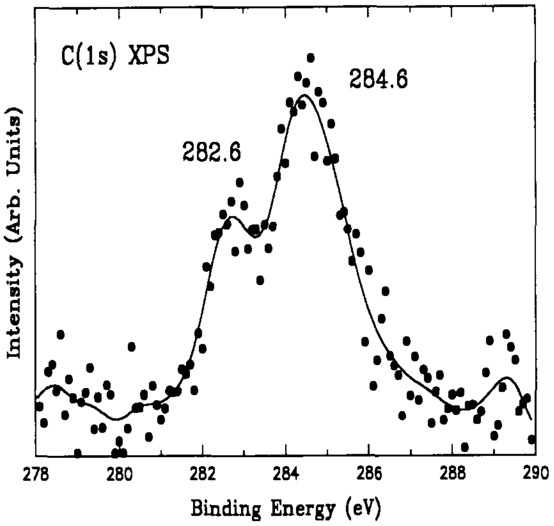

Figure 5. C(1s) XPS spectra measured after exposure of a 0.9 ML O/Mo(100) surface to methyl radicals.

surface having submonolayer oxygen coverage (0.2 ML) exhibited a sharp peak at 285.7 eV which is consistent with the binding energy reported previously for surface methoxy on Mo(110).[15]

4. Discussion

The experimental results obtained by exposing O/Mo(100) surfaces with ≥1 ML of oxygen at 300 K to the products of azomethane pyrolysis represent the adsorption and surface chemistry of methyl radicals. Adsorption of unreacted azomethane or of the side products of azomethane pyrolysis (hydrogen, nitrogen, methane, ethane, and possibly chloromethane) does not interfer since these molecules and/or their decomposition products desorb from the surface at temperatures below 300 K. The results also demonstrate that the appearance of CH_4 following methyl radical exposure is limited by a surface reaction and not by desorption. The major contributor to the hydrogen TPD was desorption from the sample holder due to pickup from the background, although a minor contribution from the sample surface is probable.

While there is no direct spectroscopic evidence from this study to establish, unambiguously, the chemical identity of the surface species formed initially by adsorbed methyl radicals at 300 K, the TPD results point strongly toward a single species with the chemical formula CH_3 rather than CH_2, CH, C, or any C_2 species. Upon heating above 300 K this surface hydrocarbon species reacts on ≥1 ML O/Mo(100) surfaces to produce mostly methane and smaller quantities of hydrogen and carbon monoxide. Clearly, CH_3 must exist on the surface, at least as an intermediate, at some point in this reaction in order for methane to be formed. Atomic carbon can be ruled out as the initial surface species at 300 K on O/Mo(100) since CO is the only product expected from this species. If the parent CH_3 decomposed to CH_2 or CH on adsorption at 300 K it is unlikely that the major reaction pathway would be hydrogenation to CH_4 under UHV conditions rather than dehydrogenation to atomic carbon and hydrogen which eventually evolved from the surface as H_2 and CO. In agreement with this argument Ko and Madix found only small amounts of methane produced following adsorption of formaldehyde (CH_2O), a CH_2-containing molecule, on clean Mo(100).[14] The low yield of C_2 compounds in TPD (<1% of CH_4) argues against a C_2 moiety as the initial surface species. Moreover, no methane was detected during TPD of adsorbed hydrocarbons containing carbon–carbon single and double bonds, ethene and propene;[10] only the parent molecule or hydrogen and CO were observed. With the exception of trimethylamine and dimethylamine,[16] methane has not been observed as a major TPD product following adsorption on O/Mo(100) of other molecules studied in this and other laboratories. The low yield of C_2H_6 also implies that diffusion of surface methyl radicals is insignificant at temperatures where the reaction proceeds and hence the carbon–surface bond is strong.

Methane desorption from oxygen-modified molybdenum surfaces occurs at 100 K and below, significantly lower than the methane produced by surface reaction of adsorbed methyl. Therefore, the desorption data in Figure 3 are controlled by the kinetics of the surface reaction rather than by methane desorption. Only two carbon-containing species, CO and CH_4, are produced by the reaction of adsorbed methyl groups and these species are produced in an approximately constant ratio of 0.3. Therefore, the integrated area under the methane desorption peak can be taken as a measure of the methyl coverage on the surface. Using the procedure of King and co-workers[17] the kinetic order for the production of CH_4 can be established from the slope of a plot of ln(methane desorption rate) vs ln(methyl coverage) at fixed desorption temperature obtained from a family of TPD curves measured at a series of initial methyl surface coverages. Slopes of approximately unity through the desorption peak were obtained from the data, indicative of a surface reaction that is first order in methyl coverage.

A sequence of reactions consistent with the observed products, the ratio of CH_4 and CO produced, and the first-order kinetics follows:

$$CH_3(ads) \rightarrow C(ads) + 3H(ads) \qquad (R1)$$

$$CH_3(ads) + H(ads) \rightarrow CH_4(g) \qquad (R2)$$

$$C(ads) + O(ads) \rightarrow CO(g) \qquad (R3)$$

$$2H(ads) \rightarrow H_2(g) \qquad (R4)$$

Reaction R1 is the decomposition of adsorbed methyl groups to produce surface hydrogen. This may be a concerted process as implied by the notation, but a sequential process is more likely. Reaction R2 is the hydrogenation of methyl to form methane. Reaction R3 is the reaction between adsorbed carbon and oxygen to form CO, and reaction R4 is the combination of adsorbed hydrogens to form H_2. Reaction R1 is a unimolecular reaction and the first step in the process. According to this scheme the formation of CH_4, CO, and H_2 are all limited by reaction R1 thereby leading to the overall first-order kinetics of the reaction. Since the ratio of CO to CH_4 yields is approximately stoichiometric in the hydrogen, reaction R4 is required to proceed to only a negligible extent. This conclusion would seem to be at odds with the observed H_2 TPD signals. However, a significant fraction of the H_2 signal originates from the sample holder, and the measured yields of CO and CH_4 are only as accurate as the mass spectrometer signal calibration, no better than 20%. In consideration of these factors, we conclude that the rate of reaction R2 is substantially faster than reaction R4, but with the present data

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we are unable to quantify the relative rates.

The breadth of the methane peak can be explained by a distribution of sites with a distribution of reaction kinetics. Adsorption on a heterogeneous distribution of sites is consistent with the rather broad C(1s) XPS peak measured for adsorbed methyl (Figure 5) and with the behavior of other molecules adsorbed on oxidized Mo(100). For example, the measured fwhm of NH_3 TPD peaks from O/Mo(100) surfaces is approximately 100 K with a peak shape similar to that of CH_4 despite the fact that NH_3 adsorbs associatively (i.e., no reaction takes place) so that molecular ammonia is the only species on the surface.[10] Similarly, CO and H_2 desorption peaks due to methanol decomposition exhibit widths >100 K even though this reaction proceeds through a single intermediate surface species (methoxy).

Within a restricted range of temperatures the surface reaction proceeds on a relatively homogeneous subset of adsorption sites. This should hold at the threshold of methane desorption so that the leading edge method of data analysis described by Habenschaden and Küppers[18] can be applied. The activation energy obtained from this method is 70 ± 3 kJ/mol. The prefactor could be obtained provided we have some estimate of the coverage of methyl groups corresponding to the subset of sites that contribute to the reaction in this temperature range. We estimate this to be on the order of 10% of the total surface coverage. Integration of the standard rate equation to simulate desorption from this state and comparison to the data in Figure 3 yields a prefactor of 10^9. These kinetic parameters are consistent with values reported in the literature for dehydrogenation of various hydrocarbons adsorbed on metal surfaces.[19] To account for the measured width of the methane desorption peaks in Figure 3 a range of activation energies spanning approximately 30 kJ/mol is required. This spread of activation energies is comparable to the difference in activation energies for dehydrogenation of C_2H_6 on Pt(111) and Pt(110)-(1×2) surfaces of 25.5 kJ/mol.[20,21] Therefore, the origin of this property for methyl dehydrogenation on O/Mo(100) may very well be structural or compositional variations in the local adsorption site.

Several pieces of evidence suggest that CH_3 bonds primarily to molybdenum to form a metal alkyl rather than to surface oxygen to form a surface methoxy on O/Mo(100). First, the measured C(1s) binding energy (284.6 eV) is less than values reported in the literature[15,22] and confirmed in our laboratory for surface methoxy (285.7 eV) formed by decomposition of adsorbed methanol. Since the surface metal atoms are less electronegative than oxygen, one might expect a lower C(1s) binding energy for methyl–metal bonding than for methyl–oxygen bonding. Moreover, our measured C(1s) binding energy is the same as the binding energy recently reported for CH_3 adsorbed on Pd(111)[23] although somewhat higher than that assigned to adsorbed methyl groups in earlier work (284.2 eV[22] on Pd(111) and 283.4 eV on Fe(100)[24]). Second, the yield of methane decreased for oxygen coverages above 1 ML where surface molybdenum is progressively blocked by oxygen but where surface oxygen remains accessible (see Figure 4). Alternatively one could argue that the chemical nature of surface oxygen at coverages above 1 ML, where oxide has been shown to form, is chemically different than at coverages below 1 ML resulting in a reduced capacity to bond methyl.

The best evidence in favor of metal–alkyl formation comes from a comparison between TPD of adsorbed methyl and methanol since the latter is known to decompose on Mo(100) via an adsorbed methoxy intermediate. The major products from methanol decomposition were CO and H_2 as observed in our laboratory and reported previously by Ko and Madix[14] and by Miles et al.[13] Adsorbed methanol produced only small amounts of CH_4 in the present work in agreement with results reported by Ko and Madix.[14] Therefore it is tempting to conclude that this methane was due to minority decomposition pathway via a metal–alkyl intermediate which was present in small concentration on the surface and not detected in the HREELS study of Miles et al.

While the comparison between adsorbed methyl and methanol provides strong chemical evidence in favor of molybdenum–methyl bonding, one could still argue that methoxy was formed by adsorption of CH_3 on O/Mo(100) but that this methoxy is not chemically identical to the methoxy formed by methanol decomposition on Mo(100) or O/Mo(100). For example, the oxygen atoms to which methyl must bond on a 1.0 ML O/Mo(100) surface are located in the 4-fold hollow sites of the Mo(100) surface and are coordinated to five molybdenum atoms: four in the first layer and one in the second layer. The vibrational spectra measured for methoxy on a variety of metal surfaces indicate oxygen bonding to one or two metal atoms corresponding to atop or 2-fold bridging geometries. If the oxygen in methoxy from methyl + O/Mo(100) is more strongly coordinated to the surface metal atoms than oxygen in methoxy from methanol + Mo(100), then it could be argued that the C–O bond is weaker in the former case with a propensity to hydrogenate and form CH_4 as a product rather than dehydrogenate and form CO and H_2. Against this argument is the fact that methane is also the primary product formed following methyl radical adsorption on Mo(100) surfaces with higher oxygen coverage where oxide formation has occurred and the oxygen must no longer be in the 4-fold hollow sites.[25] Finally, the available data do not rule out a mixture of metal–alkyl and methoxy species on the surface. The C(1s) is sufficiently broad to encompass a small amount of methoxy. Both a small amount of CO, the major product of methoxy decomposition, and methane are formed during TPD. This issue could be resolved unambiguously via the presence or absence of a C–O stretching frequency measured by surface vibrational spectroscopy.

It is interesting to consider why metal–alkyl formation is preferred over methoxy formation. A priori one could make a case for methyl adsorption on either surface molybdenum or oxygen atoms. Since the surface molybdenum atoms are electron deficient and the methyl radical is a nucleophile (low ionization potential), one might predict that methyl–molybdenum bonding would be preferred. On the other hand the carbon–oxygen bond in methoxy is exceptionally strong based on the propensity for methoxy on molybdenum surfaces to decompose by C–H bond breaking rather than C–O bond breaking. One trivial explanation would be that adsorption of methyl radicals on surface oxygen is physically blocked by surface hydrogen in the form of surface hydroxide. Surface hydroxyl groups could be formed by adsorption of either gas phase atomic hydrogen produced on hot filaments in the vacuum chamber or residual water vapor. This possibility is ruled out by the results of low exposure experiments. The yields of CH_4 and H_2 following a 0.21 L exposure are only 5.5×10^{-3} and 1.6×10^{-3} ML, respectively. Thus, even if all the hydrogen atoms required to form CH_4 and H_2 were derived from surface hydroxyl groups they would block less than 1% of the surface oxygen atoms. The available evidence suggests that the nucleophilic character of methyl radical controls the nature of the adsorption bond.

5. Conclusions

Methyl radicals adsorb on oxygen-modified Mo(100) surfaces to form surface methyl groups. The available evidence suggests that these methyl groups are bonded to surface molybdenum atoms to form a species analogous to a metal alkyl rather than to oxygen to form surface methoxy. The surface methyl groups decompose upon heating to produce surface hydrogen atoms which react rapidly with intact methyl groups to form methane which desorbs from the surface. The kinetics of this reaction are consistent with a heterogeneous distribution of methyl adsorption sites.

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