Adsorption and thermal decomposition of CH$_3$SH on the Pt(111) surface

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Adsorption, desorption and thermal decomposition of methanethiol (CH$_3$SH) on a clean and on a (2 × 2)-S covered Pt(111) surface have been studied using temperature programmed desorption, high resolution electron energy loss spectroscopy, and X-ray photoelectron spectroscopy as a function of temperature and coverage on the Pt(111) surface. Vibrational spectroscopy has been used to characterize the structure and bonding of surface intermediates formed during dehydrogenation of adsorbed methanethiol. The identity of surface intermediate species which form during thermal dehydrogenation is determined by both temperature and the availability of free Pt sites. Low coverages strongly favor low temperature dehydrogenation and decomposition reactions. Initial S–H bond activation does not occur at 110 K on crowded surfaces while complete decomposition of methanethiol is observed for 5% of a monolayer on a clean surface. For a saturated monolayer of methanethiol, XPS results indicate that about 60% of the carbon remains on the surface after heating to 750 K indicating that 40% of the carbon desorbs as CH$_4$, and C$_2$H$_4$. The fractional yield of volatile organic products increases with increasing initial coverage of methanethiol up to monolayer coverage. The structure and geometry of the adsorbed intermediates formed by CH$_3$SH decomposition also depends on coverage and temperature. Thermal dehydrogenation generates first CH$_3$S, then CH$_2$S as previously reported. In addition a new intermediate σ-bonded SCH is identified in this work. Similar species form on the (2 × 2)-S pre-sulfided surface; however, in the pre-sulfided case the S–C bonds tend to be oriented more closely along the surface normal than they are on the clean surface. Methanethiol molecules remain intact on the pre-sulfided surface up to 180 K.

1. Introduction

As part of a program to characterize molecular processes important for catalytic hydrodesulfurization (HDS) [1] we have undertaken a study of the adsorption and thermal decomposition of methanethiol on the Pt(111) surface. Because of their structural simplicity, thiols have been used extensively to model hydrodesulfurization processes on surfaces. Adsorption and decomposition of thiols has been studied on a number of well characterized transition metal surfaces using a combination of surface sensitive spectroscopies to characterize the structure and bonding of the surface intermediates formed during thermal decomposition. Particular attention has been focused on the adsorption and decomposition of CH$_3$SH on a number of metallic single crystals because the simplicity of the intermediates formed makes detailed interpretation of spectroscopic results feasible. We have previously reported that methylthiolate and methylene sulfide surface intermediates are formed during decomposition of methanethiol on the Pt(111) surface [2]. Since our original report, methanethiol adsorption and decomposition has been characterized on Ni(100) [3,4], Ni(110) [5], Ni(111) [6], Fe(100) [7], Cu(100) [8], Cu(111) [4,9], Au(111) [10], and W(211) [11] surfaces. Thermal decomposition of higher thiols

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(C_2-C_5) on the Mo(110) surface have recently been studied by Roberts and Friend [12–16]. For all of the thiols on these metallic single crystal surfaces, low temperature S–H bond cleavage results in the formation of the corresponding adsorbed thiolate bound to the surface through the S atom. This initial dehydrogenation process is followed by a series of dehydrogenation processes which depend on the adsorbate coverage, identity and structure of the surface.

In this work, the adsorption and decomposition of CH_3SH on a clean and sulfided Pt(111) surface have been investigated using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and X-ray photoelectron spectroscopy (XPS). This report substantially extends our previous discussion [2] which focused on identification of the two primary surface intermediates formed during methanethiol decomposition on the Pt(111) surface using HREELS and NEXAFS. Additional structural characterization of the methylthiolate and methylene sulfide intermediates based on a series of detailed XPS and HREELS experiments is presented. The effects of initial coverage, isotopic substitution and pre-adsorbed sulfur on methanethiol adsorption and decomposition are presented in detail.

The S–H bond in adsorbed molecular CH_3SH is broken at low temperature resulting in the formation of adsorbed hydrogen and methylthiolate as is the case for most adsorbed thiols. Both HREELS and NEXAFS results reported earlier [2] suggest that the C–S bond in adsorbed CH_3S is tilted by about 45° relative to the surface normal. A tilt of 60° has also been reported for the C–S bond in CH_3S on the Cu(111) surface [17]. At 380 K selective loss of a methyl hydrogen results in the formation of the methylene sulfide (CH_2S) intermediate, where the C–S bond lies about 20° from the surface. In contrast, Sexton's work concerning methanol adsorption and decomposition on the clean Pt(111) surface finds no evidence for adsorbed formaldehyde (CH_2O) or even methoxy species (CH_3O) above 140 K, instead complete decomposition to adsorbed CO and atomic hydrogen dominates [18]. A good comparison between the reactions of methanol

and methanethiol on clean, oxided, sulfided and carbided W(211) surface was made by Benziger and Preston [11]. On the clean W(211) surface, methanol and methanethiol form analogous surface intermediates. However, on the sulfided W(211) surface CH_3SH adsorbs by forming a disulfide intermediate $-SSCH_3$, while CH_3OH adsorption is inhibited.

Recent studies of methanethiol adsorption on Ni(100) [3,19] and Ni(110) [5] surfaces also indicate the formation of methylthiolate at low temperatures. However, no evidence for a CH_2S intermediate was observed on either surface. Angle resolved photo emission (ARUPS) studies [4] of methanethiol and dimethyl disulfide (CH_3S-SCH_3) decomposition also indicate that CH_3S is the primary stable intermediate on both Ni(100) and Cu(111) surfaces at room temperature. Methylthiolate has also been widely observed as a ligand in organometallic coordination compounds of transition metals [20].

2. Experimental

The experiments were performed in a UHV chamber with a background pressure of $\sim 1 \times 10^{-10}$ Torr. All the surface techniques were located on a single level so that a simple rotation about the manipulator axis was sufficient to position the sample in front of each spectrometer or source. The fixed geometry HREELS spectrometer was mounted on a 10 inch flange with both monochromator and analyzer on the same side of the sample. The accuracy of the measured vibrational frequencies was ± 10 cm^{-1}. XPS was performed with a hemispherical analyzer and an Al Kα X-ray source. An electron gun operating at grazing incidence was used with the hemispherical analyzer for AES.

The ionizer of the quadrupole mass spectrometer was enclosed in a gold-plated cylinder with a coaxial entrance tube. The sample was positioned 1 mm in front of this tube for the thermal desorption spectra so that only molecules desorbing from the flat surface region could enter the ionizer through the coaxial tube. The desorption spectra were measured with a multiplexer that

allowed simultaneous monitoring of up to seven masses.

The Pt(111) sample was attached to an L-shaped manipulator that provided the usual 3-coordinate displacements and a full 360° rotation about the manipulator axis. A limited polar rotation ($+15°$, $-60°$) about the vertical axis on the surface plane was also available. The sample was cooled to 100 K with an internal liquid nitrogen reservoir and was heated to 1500 K by passing a DC current through two 0.5 mm Ta support wires that were spot-welded to the back face of the crystal. A 0.08 mm chromel–alumel (type K) thermocouple spot-welded to the sample edge was used for temperature measurement and feedback control of the programmed temperature ramp.

The crystal was cleaned of carbon, sulfur, and calcium oxide by the usual procedures of Ar ion bombardment, high-temperature annealing and O_2 treatments. The (2×2)-S structure with a coverage of 0.25 ML was prepared by saturating the clean surface with H_2S at 110 K and then heating to 500 K. Exposing the sample to an S_2 flux produced by electrochemical decomposition of Ag_2S yielded identical results for the S-covered surfaces and we will not specify the preparation used in the following sections.

The exposures to gases (H_2S, CH_3SH, or CD_3SD) were performed with individual leak valves. After passing the leak valve, the gases were directed near the sample surface by tubes terminated with microchannel arrays. The directional nature of the gas stream obtained in this way produced high local pressures ($\sim 10 \times$) at the crystal. In this work we measured exposures with the more sensitive mass-spectrometer signal.
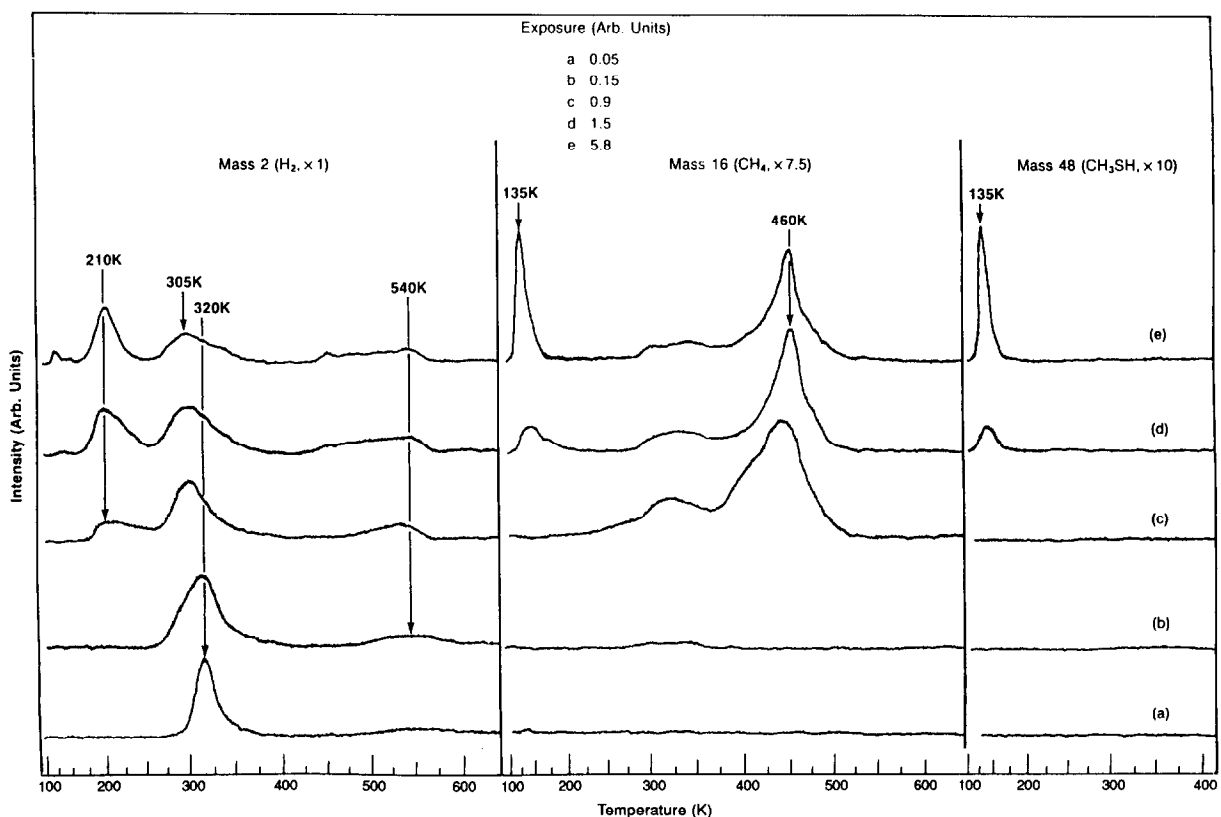

Fig. 1. TPD profiles for hydrogen, methane and methanethiol as a function of CH_3SH exposure on the Pt(111) surface. $T_A = 110$ K, $\beta = 10$ K/s.

We define our arbitrary exposure units so that one unit of exposure to CH_3SH produced a saturation first-layer coverage on the clean Pt(111) surface.

3. Results and discussion

The "temperature programmed decomposition of methanethiol monolayers" section 3.1 summarizes the structure of the surface intermediates formed by partial dehydrogenation of methanethiol as an aid in organizing the spectroscopic data presented in the following sections. The "HREELS of the saturated monolayer during thermal decomposition" section 3.2 summarizes a series of thermal annealing experiments for a saturated monolayer where the surface intermediates have been characterized by vibrational spectroscopy. The "HREELS of submonolayer coverages" section 3.3 summarizes the coverage and temperature dependence of surface intermediates formed from submonolayer coverages using vibrational spectroscopy. The "XPS" section 3.4 discusses the characterization of dehydrogenated surface intermediates using X-ray photoemission spectroscopy. The "CH₃SH adsorption on a sulfur monolayer" section 3.5 discusses the effect of adsorbed sulfur on thermal decomposition of methanethiol.

3.1. Temperature programmed decomposition of methanethiol monolayers

Sequential dehydrogenation of methanethiol on the platinum (111) surface results in the formation of first methylthiolate, then methylene sulfide, and then further dehydrogenated intermediates as discussed previously [2]. These dehydrogenation reactions result in the desorption of hydrogen and methane into the gas phase. A small amount of ethylene desorbs from the surface along with a high temperature methane peak. All of the adsorbed sulfur and about 60% of the adsorbed carbon remain on the surface after cycling to high temperature. Molecular methanethiol (mass 48) sublimes at 135 K for initial coverages larger than a monolayer (ML). The appear-

ance of this molecular methanethiol desorption peak was used as a reference point to calibrate the exposure which corresponds to one monolayer.

In fig. 1, we show TPD spectra corresponding to a series of initial exposures of methanethiol ranging from 0.05 to 5.8 monolayer exposure units. After completion of a monolayer (curves c and d) the primary methane peak occurs at 460 K; however, a small methane peak at 320 K persists as indicated in fig. 1. H_2 desorption peaks for monolayer thiol coverages are observed at 210, 305, 460 and 540 K. These hydrogen peaks correspond to desorption of hydrogen from cleavage of the S–H bond (210 K), the initial reactions of methylthiolate (305 K), the disproportionation of the methyl group in methylene sulfide (460 K) and finally dehydrogenation of methylene sulfide (540 K). The hydrogen peak at 210 K occurs at a unusually low temperature. We believe that this low temperature results from increased repulsive interactions between adsorbed atomic hydrogen and high coverages of coadsorbed surface species. A similar temperature decrease was observed for D_2 coadsorbed with hydrocarbons on the same Pt surface [21,22].

At exposures below 0.25 ML (curves a and b in fig. 1), H_2 is the major product observed, with a peak around 320 K which is similar to desorption of H_2 from a clean Pt(111) surface. This result suggests that the 320 K H_2 peak is a desorption limited peak. A smaller hydrogen peak is also observed around 540 K. A small amount of CH_4 is also observed between 300 and 340 K. Thus at low coverage, complete dehydrogenation is the primary reaction pathway observed since hydrogen is the primary desorption product observed. Complete decomposition of methanethiol at low coverage has also been observed on other metals [3,5,19].

3.2. HREELS of the saturated monolayer during thermal decomposition

The structure of the surface species that form following methanethiol adsorption and thermal decomposition has been investigated using vibrational spectra taken with HREELS. All the elec-
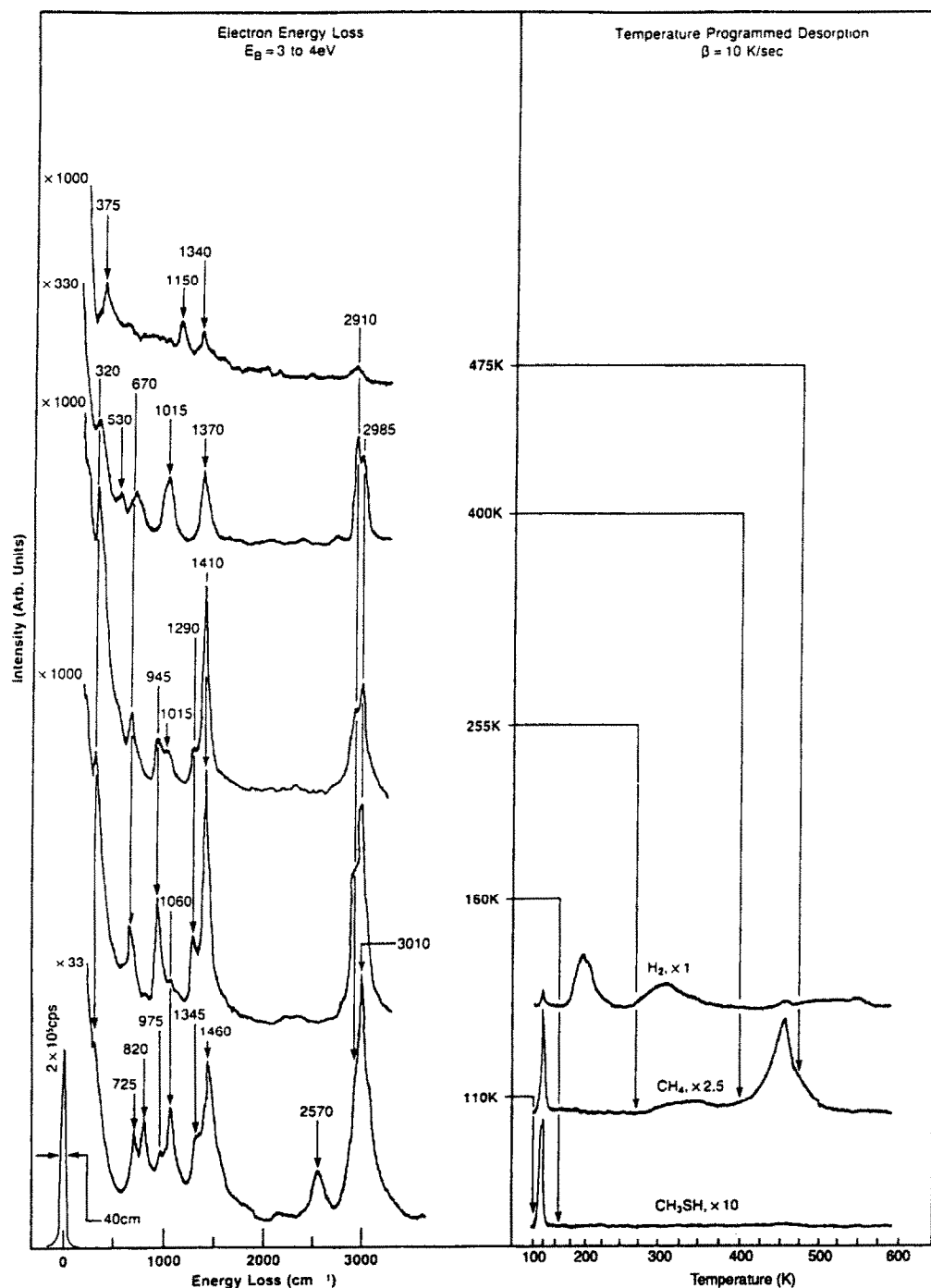
Fig. 2. Left: HREEL spectra and their corresponding dominant surface species for various stages of the reaction following multilayer exposure of CH_3SH on Pt(111) surface. All spectra were taken when the sample was cooled down to 110 K from the indicated temperatures. Right: TPD spectrum to indicate the point where the HREELS were obtained.

tron energy distribution presented in this work was collected in the specular direction. The vibrational spectra of intermediates formed by thermal decomposition of the adsorbed methanethiol were obtained by heating to the specified decomposition temperature and then quenching the sample so that vibrational spectra could be obtained. Decomposition temperatures were selected based on the TPD results.

3.2.1. Condensed multilayers of CH₃SH at 110 K

The vibrational modes of multilayer CH_3SH match the gas phase IR frequencies and thus can be assigned to the frequencies of intact molecular CH_3SH. The vibrational spectrum shown in fig. 2 was obtained from a multilayer of molecular methanethiol by exposing the clean surface to approximately 6 times the amount of CH_3SH required to complete a monolayer. Unfortunately, after deposition of multilayer methanethiol at 110 K, the resolution of our HREELS spectrometer is reversibly degraded from 40 to 80 cm^{-1}. The vibrational transitions observed from the multilayer and adsorbed surface species formed by methanethiol decomposition are summarized in table 1 together with the reference gas phase IR data [23] and spectroscopic assignments. Deviations from the gas phase frequencies [23–25] are not larger than 20 cm^{-1}. Notice also that the two C–H deformation peaks (1460 and

1345 cm^{-1}) have an intensity ratio clearly larger than one, as a result of the overlap of the two asymmetric modes A' and A" with gas phase frequencies of 1430 and 1475 cm^{-1}. Asymmetric modes can be excited in the multilayer because of the relaxation of the dipole selection rule far from the surface. These vibrational modes are characteristic of intact molecular CH_3SH overlayers.

All the vibrational assignments are supported by the isotope shifts observed from CD_3SD on the Pt(111) surface. As shown in table 1, the modes associated with hydrogen undergo downshift in the case of the deuterated thiol (figure not shown). The energy resolution in the case of CD_3SD (65 cm^{-1}) was not high enough to resolve the two CD_3 rocking and the two CD_3 deformation modes. Nevertheless, the general trend of the modes is in good agreement with the corresponding gas phase CD_3SD IR frequencies [26] with the exception of the symmetric C–D stretch (A') which showed an upward shift of about 45 cm^{-1}.

3.2.2. Partial dehydrogenation of a saturated monolayer at 160 K

Heating the sample to 160 K causes desorption of condensed CH_3SH multilayers as shown in the first curve in fig. 2. The spectroscopic resolution increases (to 40 cm^{-1}) after this multilayer

Table 1
Vibrational mode assignments for multilayer methanethiol on Pt(111) at 110 K [a]

ν(H) [b]	ν(D) [c]	ν(H)/ν(D)	Assignment	Type (C_s)	Gas phase [d]
320	320	1	z-frus.trans.		
725	680	~ 1	ν(C–S)	A'	708
820	680	1.21	ρ(S–H)	A'	805
975	765	1.27	$\rho(CH_3)$	A'	976
1060	765	1.42	$\rho(CH_3)$	A"	1074
1345	1040	1.29	$\delta(CH_3)$	A'	1335
1460	1040	1.40	$\delta(CH_3)$	A"	1430
				A'	1475
2570	1850	1.39	ν(S–H)	A'	2597
2910	2195	1.33	ν(C–H)	A'	2930
2985	2255	1.32	ν(C–H)	A'	3000
3010	2260	1.33	ν(C–H)	A"	3000

[a] All frequencies in cm^{-1}.
[b] Vibrational frequencies for adsorbed CH_3SH.
[c] Vibrational frequencies for adsorbed CD_3SD.
[d] Gaseous CH_3SH, ref. [23].

methanethiol desorbs. The two characteristic S–H losses at 2570 (stretch) and 820 cm^{-1} (bend) are removed from the spectrum. This result indicates that after annealing to 160 K molecular CH$_3$SH no longer remains on the surface. The remaining vibrational modes are similar to those from the undissociated molecule except for a general downward shift in frequency between 15 and 50 cm^{-1}. This spectrum is characteristic of adsorbed methylthiolate (CH$_3$S). The low frequency peak observed at 320 cm^{-1} remains essentially unchanged and is attributed to the Pt–SCH$_3$ stretching mode. In the low frequency region, the molecular methanethiol C–S stretching mode at 725 cm^{-1} shifts to 670 cm^{-1}. An enhancement of the 1410 cm^{-1} loss relative to 1290 cm^{-1} in the deformation mode region is also observed. In the rocking mode region, the A″ asymmetric loss at 1060 cm^{-1}, intense in the multilayer case, decreases in intensity relative to that of the 975 cm^{-1} peak. The 1290 cm^{-1} loss, which corresponds to the symmetric CH$_3$ deformation mode in C$_3$-type CH$_3$ groups ("flower mode"), is less intense than the 1410 cm^{-1} mode. The change in intensity in the deformation modes together with the observation of the two rocking modes in the spectrum is a clear indication of the reduced symmetry of the adsorbed species, namely a CH$_3$S–Pt with a tilted S–C axis.

The HREELS data presented above indicate that adsorbed methylthiolate is formed on the surface since both the SH bending and stretch modes disappear, while modes characteristic of the thiolate remain. Several modes shift in frequency by up to 45 cm^{-1} because of interactions with the surface. These results indicate that the CH$_3$S–Pt species retains a C$_s$ symmetry.

3.2.3. Partial dehydrogenation of a saturated monolayer at 255 K

Heating the sample to 255 K produces the vibrational spectrum shown in the third curve of fig. 2. Table 2 summarizes the vibrational frequencies observed as a function of annealing temperatures. H$_2$ formed from the SH hydrogen desorbs at 210 K. The vibrational spectrum observed at 255 K is very similar to the spectrum taken following partial dehydrogenation at 160 K.

The Pt–SCH$_3$ stretching mode at 320 cm^{-1} and the C–S stretching mode at 670 cm^{-1} remain essentially unchanged. NEXAFS results at 255 K [2] show an approximate tilt angle of 45° between the S–C bond and the flat Pt(111) surface for methylthiolate.

A new loss peak at 530 cm^{-1} is also observed which may be associated with a Pt–C stretching mode. As indicated in the next section, the methylene sulfide (CH$_2$S) species is the next stable intermediate formed during partial dehydrogenation. In adsorbed monolayers, the surface dipole selection rule [27] forbids A″ modes, like the 1060 cm^{-1} mode due to a CH$_3$ rocking. The observed small peak may be the result of impact scattering or may be caused by initial stages of thiolate (CH$_3$S) dehydrogenation to form methylene sulfide (CH$_2$S) which shows a strong CH$_2$ wagging mode at 1015 cm^{-1}. Thus even at 255 K the initial stages of dehydrogenation may be occurring for a small fraction of the adsorbed methylthiolate:

$$CH_3S-Pt \rightarrow Pt-CH_2S-Pt + \tfrac{1}{2}H_2.$$
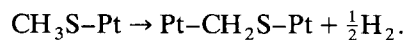
The increase in the intensity of the 1015 cm^{-1} peak observed in fig. 2 is also consistent with the appearance of the dipole enhanced CH$_2$ wagging mode at this frequency. However, the vibrational spectrum clearly shows that the dominant surface species remains methylthiolate at 255 K.

3.2.4. Partial dehydrogenation of a saturated monolayer at 400 K

Further heating of the surface to 400 K results in dehydrogenation of the adsorbed methylthiolate to form adsorbed methylene sulfide (CH$_2$S) [2]. As shown in figs. 1 and 2, H$_2$ (305 K) and a small amount of CH$_4$ (320 K) desorb when the surface is heated to 400 K. Therefore, both C–H and C–S bond breaking processes must be occurring in this temperature range.

The vibrational spectrum obtained after thermal processing to 400 K is shown in fig. 2. Table 2 summarizes the various vibrational modes observed following partial dehydrogenation at 400 K. The distinct Pt–C stretch frequency observed at 530 cm^{-1} after heating to 400 K suggests either a bidentate species Pt–SCH$_2$–Pt with a C$_s$

Table 2
Vibrational mode assignments following thermal processing of multilayer methanethiol on Pt(111) [a]

255 K	400 K	475 K	Assignment
320	320		$\nu(Pt-SCH_{2,3})$
		375	$\nu(Pt-S)$
530	530	550	$\nu(Pt-CS(Pt)H_x)$, $\nu(C=S)$,
670	670		$\nu(C-S)$
945			$\rho(CH_3)$
1015	1015	1150	$\rho(CH_3)$, $\rho(CH_2)$wag
1290			$\delta(CH_3)$ A'
	1370	1340	$\delta(CH_2)$ A'
1410			$\delta(CH_3)$ A''
2910	2910	2910	$\nu(C-H)$
2985	2985		$\nu(C-H)$
3010			$\nu(C-H)$

[a] All frequencies in cm⁻¹.

symmetry or dissociation to form adsorbed C or CH groups. The molecular methylene sulfide intermediate is favored by a previous NEXAFS study of this same system at 380 K which indicated a tilt angle of 20° with respect to the Pt(111) surface [2]. We observe a decrease in intensity of the peaks at 3000 cm⁻¹ relative to the 2910 cm⁻¹ peak. Because of the absence of CH stretch modes above 3000 cm⁻¹ which would indicate the presence of sp² hybridized S=CH₂, we prefer the σ-bonded bidentate Pt-SCH₂-Pt configuration. The loss of one H atom to form CH₂ reduces the number of modes observed in the CH stretching region to two, the A' mode at 2910 cm⁻¹ and the A'' mode at 2985 cm⁻¹. The CH deformation region (1300–1500 cm⁻¹) now contains only one peak at 1370 cm⁻¹ instead of two, indicating the dominance of CH₂ groups instead of CH₃ groups. Likewise, in the rocking region a single peak at 1015 cm⁻¹ remains which corresponds to an A' type wagging mode of CH₂.

We believe that the C–S bond breaking processes at 320 K primarily involves reaction between methylthiolate and coadsorbed hydrogen from methanethiol decomposition. The C–S bond breaking reaction that produces CH₄ at 320 K leaves atomic S on the surface. The Pt–S stretch mode occurs at 375 cm⁻¹ as indicated by previous studies with H₂S [28]. Because of the low concen-

tration of atomic sulfur, this loss may not be resolved until thermal processing beyond 460 K which removes interfering species and makes this spectral region accessible.

3.2.5. Partial dehydrogenation of a saturated monolayer at 475 K

An adsorbed monolayer of methanethiol was further dehydrogenated at 475 K. As shown in fig. 1, the primary CH₄ peak occurs at 460 K indicating that C–S bond activation is an important process in this temperature range. The loss spectra shown in the top curve in fig. 2 indicate the presence of some residual intensity in the C–H stretch and deformation regions, at 2910 cm⁻¹, 1150 and 1340 cm⁻¹. The C–S stretching mode at 670 cm⁻¹ disappears and a new peak at 375 cm⁻¹ appears in place of the 320 cm⁻¹ peak.

The adsorbed intermediates formed after methane desorption at 460 K are difficult to assign unambiguously because of small concentrations and the complexity of the species. A substantial amount of adsorbed atomic sulfur remains on the surface after heating to 475 K as indicated by the pronounced 375 cm⁻¹ Pt–S stretching mode observed (fig. 2). A small peak at 550 cm⁻¹ is caused by a Pt–C stretching mode. A weak 2910 cm⁻¹ loss is the only visible C–H stretch mode, while the 2985 cm⁻¹ C–H stretch is no longer observed. The 2910 cm⁻¹ frequency observed for the C–H stretching mode argues in favor of sp³ hybridization for at least some of the remaining C–H containing species. The $\nu(Pt-C)$ frequency observed is too high to be direct bonding of the carbon atom in the three-fold hollow site. The presence of modes at 1150 and 1340 cm⁻¹ indicates that adsorbed CH₂ containing groups are still present on the surface. The small amount of H₂ evolving at 540 K is likely to be the result of the complete dehydrogenation of adsorbed S–CH$_x$, (x = 1 or 2). We cannot rule out the possibility that some surface C–C dimers containing hydrogen may be present since small amounts of ethylene are observed at lower temperature. Salmeron and Somorjai have also reported that the dehydrogenation of hydrocarbons on Pt surfaces results in H₂ peaks being formed in the temperature range 300 to 700 K [21,22].

3.2.6. Partial dehydrogenation of a saturated monolayer at 600 K

Heating the sample to 600 K (figure not shown) produced only two surface species: atomic S and C, as judged by the Pt–S and Pt–C stretching frequencies at 375 cm^{-1} and 530 cm^{-1} respectively. The ν(Pt–S) loss is in good agreement with the 375 cm^{-1} stretching mode in the (2×2)-S
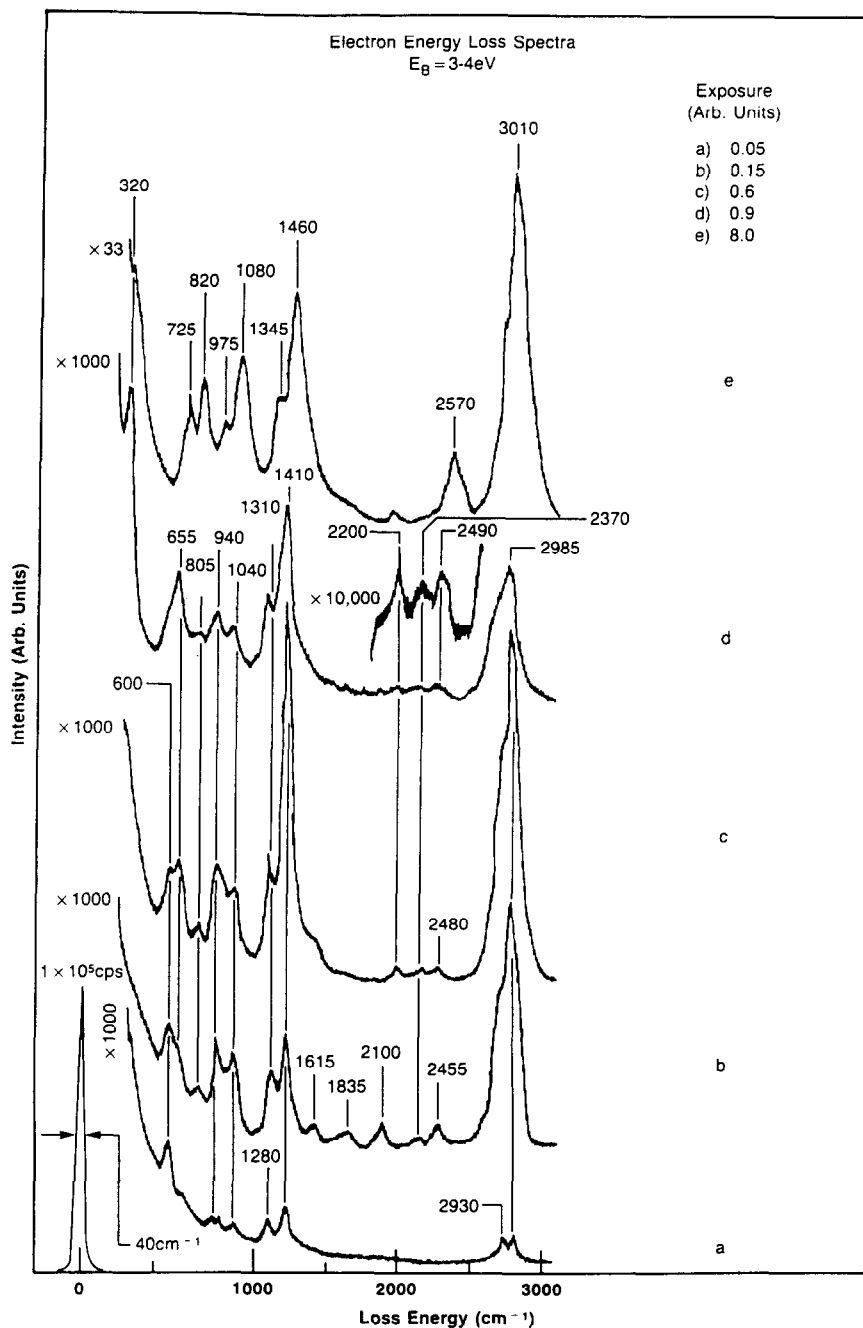

Fig. 3. HREEL spectra of CH₃SH on Pt(111) at 110 K for various coverages of methanethiol.

structure where the sulfur is adsorbed in a three-fold hollow site [28]. This similarity suggests that the thiolate adsorption site may be similar. However, the nearest-neighbor force constant model [27], indicates that the modification of vibrational frequencies for different adsorption sites (e.g., top, bridge or three-fold site) for a large atom like S may be quite small. Intuitively, however, the S is most likely to occupy the energy site with maximum coordination number, which is the three-fold symmetry.

3.3. HREELS of submonolayer coverages

Substantial changes in the stability of methanethiol and derived intermediates species are also observed as a result of changes in initial coverage at 110 K. Fig. 3 summarizes the loss spectra for the adsorbed methanethiol as a function of methanethiol exposure. Curve e at the top of this figure corresponds to condensed multilayers (similar to the low temperature spectrum in fig. 2). The remaining curves, a to d, correspond to less than a monolayer coverage.
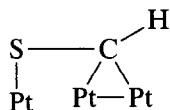
In general, dehydrogenation is initiated at lower temperature for low coverages of methanethiol. The availability of clean reactive surface sites may play an important role in promoting low temperature reactions. At high coverage both crowding of the surface species and reductions in the reactivity of metal sites by nearby adsorbates may reduce the reactivity of the metal surface.

For coverages below about 5% of saturation (curve a in fig. 3), no S–H stretch or bending modes are observed following adsorption at 110 K indicating that the S–H bond breaks on adsorption. The higher intensity of the CH_3 deformation loss at 1310 cm^{-1} relative to the 1410 cm^{-1} may indicate that the C–S axis in the methylthiolate forms a larger angle with the Pt surface as compared to the high coverage case. No high energy shoulder is observed in the CH stretch region though, indicating that S=CH_2 type species are not formed under these conditions. Assignment of the peak at 600 cm^{-1} is not clear-cut at this point. We believe this mode may be caused by a Pt–H stretching mode resulting from

hydrogen from methanethiol decomposition. Baro et al. [29] reported a ν(Pt–H) value of 550 cm^{-1} for free hydrogen on clean Pt(111) surface. This loss can not be resolved in the saturated case since it is dominated by the more intense C–S stretch mode (curve d, fig. 3). With increasing temperature, this 600 cm^{-1} mode disappears as may be expected, since hydrogen desorbs at 210 K.

At 15% coverage, the concentration of free Pt sites has decreased and undissociated molecules are stable on the surface as shown by the presence of S–H stretching and bending modes in spectrum b, fig. 3. The thermal dehydrogenation of this partially covered surface is quite different than thermal dehydrogenation of a methanethiol saturated surface. With increasing temperature, the bending (805 cm^{-1}) and stretching (2520 cm^{-1}) frequencies of SH disappear. We believe that the surface species generated by heating the 15% saturated Pt surface to 255 K consists of a mixture of methylthiolate and methylene sulfide. For this partially dehydrogenated surface at 255 K the 600 cm^{-1} mode disappears and a new mode appears at 545 cm^{-1}. The rocking and deformation components at 1310 and 940 cm^{-1} are substantially reduced in intensity while the primary doublet peaks at 1005 and 1390 cm^{-1} remain quite intense. The low frequency shoulders observed in the CH_3 deformation region (940 and 1310 cm^{-1}) suggest that a small amount of CH_3S still remains. The intensity of the 3010 cm^{-1} loss decreases relative to the 2915 cm^{-1} loss and a new high energy shoulder appears in the C–H stretching region (3070 cm^{-1}). The presence of the 3070 cm^{-1} shoulder in the C–H stretching region argues strongly in favor of the existence of sp^2 hybridized carbon, therefore we propose a π-bonded S=CH_2 surface intermediate at low coverage. We also observe the appearance of a 545 cm^{-1} loss which we attribute to a Pt–C stretching mode (one Pt atom). The intensity of the 1005 cm^{-1} mode is also substantially larger than expected from adsorbed methylthiolate in the CH stretching region. Together this evidence indicates that several species may coexist on the surface including CH_3S and several types of CH_2S.

Continued heating to 385 K results in new features in the HREELS spectrum. The Pt–C mode decreases in frequency from 545 to 475 cm^{-1} suggesting that the Pt–C coordination increases. The weak 660 cm^{-1} loss confirms the existence of S–C bonds on the surface at 385 K. The 800 cm^{-1} peak can be interpreted as a CH rocking frequency, whereas the single CH stretch peak indicates that one single H atom is bound to the C. The frequency of 2965 cm^{-1} indicates sp^3 hybridization. We propose the σ-bonded structure indicated below for this intermediate at 385 K:

$$
\begin{array}{c}
\text{S}\!-\!\!-\!\!-\text{C}\overset{\displaystyle/\text{H}}{\underset{/\backslash}{}} \\
\mid \qquad /\backslash \\
\text{Pt} \quad \text{Pt}\!-\!\text{Pt}
\end{array}
$$

This species seems to be important at low coverages; however, small coverages of this species may also still be present in the monolayer experiments. The losses due to SCH in that case could be masked by the more intense losses at similar positions due to SCH$_3$ and SCH$_2$ species. For monolayers at higher temperatures (> 460 K), modes from this species may be observed as suggested in the previous section.

3.4. XPS of the saturated monolayer during thermal decomposition

The evolution of the C 1s and the S 2s core level photoemission peaks as a function of partial thermal decomposition on the Pt(111) surface saturated with CH$_3$SH are shown in fig. 4. For condensed multilayers the C and S peaks appear at 285.1 eV for C 1s and 227.8 cV for S 2s with their highest binding energies. This C 1s peak position is higher (by about 0.5 eV) than that observed for CH$_n$ groups [7]. The S 2s peak, after accounting for a shift of 65.1 eV in going from 2p to 2s, is in good agreement to that quoted for solid C$_6$H$_5$SH [30], which also contains a thiol sulfur.

After multilayer desorption (180 K) there is a 0.9 eV downward shift in BE for C and 1.0 eV for S. A large part of this shift is simply due to the increased metal screening of the core holes of the first layer molecules as compared to solid methanethiol multilayers. At 284.2 eV, the monolayer C peak is close to that reported for CH$_n$ groups. After heating to 385 K, the C 1s peak shifts again by 0.7 eV to a lower BE of 283.5 eV. This shift is accompanied by a 10% loss in the
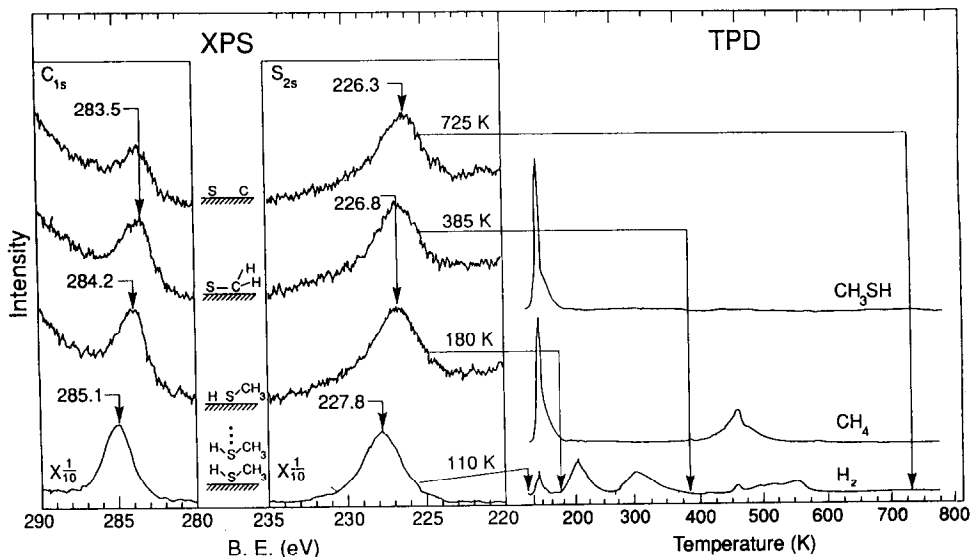

Fig. 4. XPS data showing the C 1s and S 2s core levels for various stages of the reaction following multilayer exposure of CH₃SH on Pt(111) at 110 K. All spectra were taken when the sample was cooled down to 110 K from the indicated temperatures.

peak area relative to the monolayer. The S 2s peak shows no noticeable changes with increasing temperature and remains at 226.8 eV. Heating to 725 K removes all H_2 and CH_4 resulting in a 40% decrease in the C 1s peak area relative to the monolayer. The carbon core level remains at 283.5 eV which corresponds to carbon bound to

the Pt metal. The S 2s peak shows a shift of 0.5 to 226.3 eV with a 10% attenuation.

Heating of the sample to 385 K causes the desorption of hydrogen and small amount of methane as indicated by the TPD and changes in the C 1s peak area. The adsorbed thiolate undergoes dehydrogenation to form adsorbed methy-
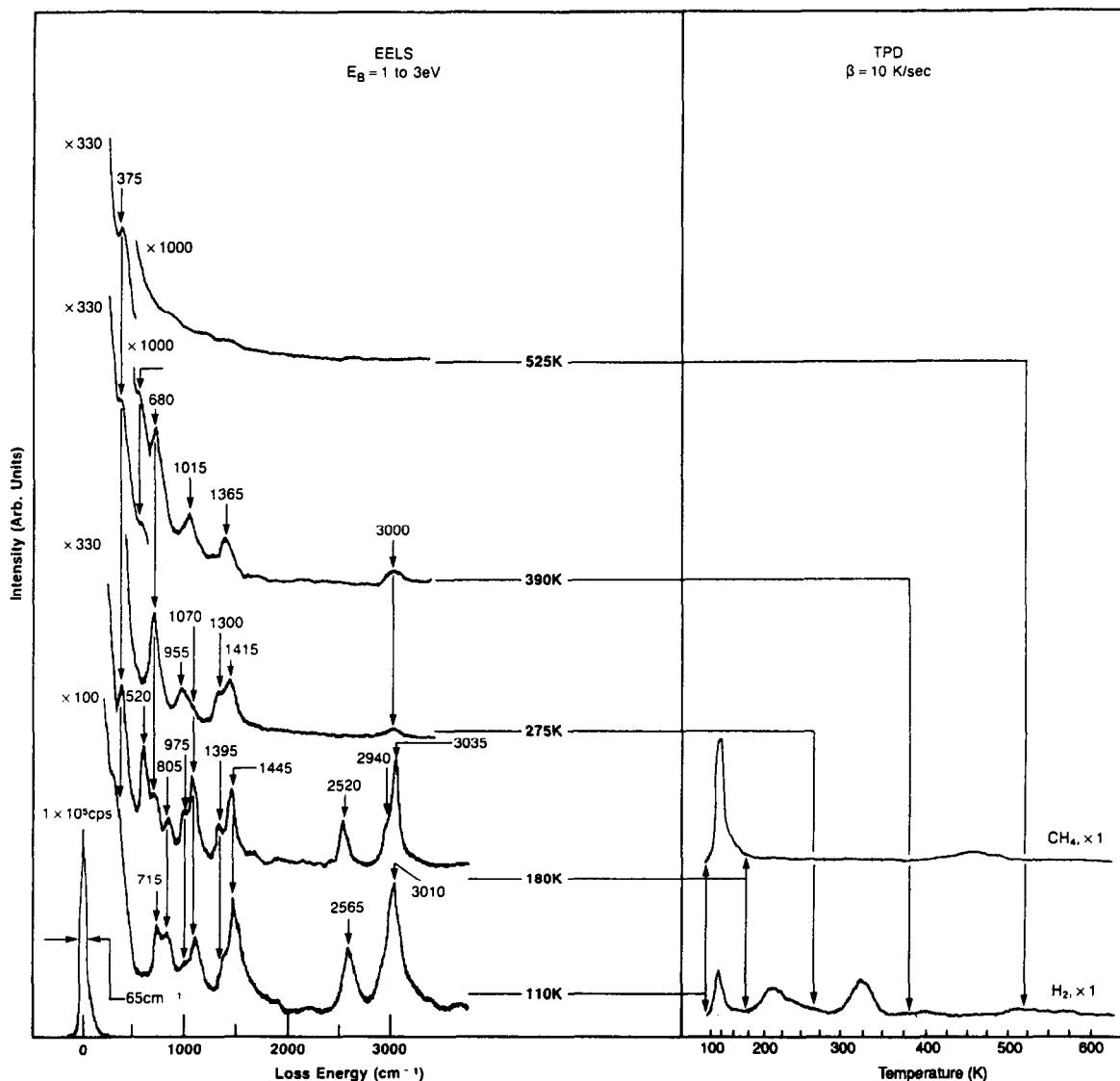

Fig. 5. Left: HREEL spectra for various stages of the reaction following multilayer exposure of CH₃SH on the (2 × 2)-S pre-adsorbed Pt(111) surface. All spectra were taken when the sample was cooled down to 110 K from the indicated temperatures. Right: Supporting TPD spectrum.

lene sulfide (SCH$_2$) this change in chemical structure causes a downshift in the C 1s binding energy from 284.2 to 283.5 eV indicating increased interaction of the carbon with the platinum surface. This shift is consistent with the vibrational results since the sulfur does not change substantially while the carbon interacts more strongly with the surface. Heating the sample past the methane desorption temperature of 460 K results in 40% attenuation in the C 1s peak relative to the monolayer. No energy shift in the C core level is observed in this process indicating that the carbon is still bonded to the Pt surface. The sulfur 2s peak, on the other hand, shows little change in area and a shift of 0.5 eV. The shift in position indicates that the C–S bond has broken in agreement with the vibrational results. The XPS intensity indicates almost all the sulfur remains on the surface as atomic sulfur at 725 K.

3.5. CH₃SH adsorption on a sulfur monolayer

At 110 K, condensed multilayer methanethiol on the (2 × 2)-S covered Pt(111) surface has vibrational modes characteristic of molecular gas phase CH$_3$SH as indicated by the bottom curve in fig. 4. Heating this surface to 180 K removes the condensed multilayers and produces a monolayer loss spectrum with S–H stretching (2520 cm^{-1}) and bending modes (805 cm^{-1}) indicating that intact methanethiol molecules remain on the pre-sulfided surface up to 180 K. This result is in marked contrast to low coverage methanethiol on the clean Pt surface (fig. 3), where most of the S–H bonds are broken even at 110 K. The S–H modes are substantially more intense on the sulfided surface than on the bare Pt surface (fig. 3) perhaps indicative of a different S–H orientation on the sulfided surface. The doublet peaks in the C–H deformation and rocking regions are also clearly visible at frequencies similar to previous spectra on the bare Pt surface. The stretching modes for the S–C bond at 680 cm^{-1}, and the Pt–S bond at 375 cm^{-1} are also clearly visible. A new intense peak at 520 cm^{-1} is most likely due to a Pt–C stretching mode.

Heating to 275 K results in S–H bond breaking and subsequent desorption of the hydrogen

(220 K) as seen in the TPD and HREELS spectra shown in fig. 5. The two S–H modes are completely removed from the loss spectrum after the hydrogen desorbs. A definite reduction of intensity in the CH stretching region is also observed. A strong S–C stretching mode is observed at 680 cm^{-1}. The deformation and rocking modes are still present in the form of doublets, although, in each case, loss of intensity of the higher frequency component is visible. The 520 cm^{-1} Pt–C stretching mode has also disappeared. Since no methane desorbs from monolayer methanethiol, the increase in intensity of the S–C stretch at 680 cm^{-1} and the absence of the Pt–C stretch at 520 cm^{-1} suggests a possible change in orientation of the S–C bond. The S–C bond appears to be reoriented towards the surface normal. This geometry is also consistent with the decrease in the relative intensity of the 1070 cm^{-1} loss compared to the 955 cm^{-1} mode.

Heating to 390 K produces spectra similar to those from a saturated monolayer on the clean Pt surface when heated to 400 K (fig. 2), except that the C–H stretching intensity is much smaller. This difference again suggests a vertical orientation of the S–C bond on the pre-sulfided surface in contrast to the tilted orientation on the clean Pt(111) surface. Heating to 390 K causes the desorption of H$_2$ at 305 K, in an amount similar to the first peak at 220 K. No CH$_4$ is evolved from the sulfided surface below 305 K. The loss spectrum shows the change of the doublet to a singlet structure in the CH deformation and rocking regions while the S–C stretching mode is still clearly visible. Further heating to 525 K results in CH$_4$ evolution and the disappearance of all losses except for the Pt–S stretching mode at 375 cm^{-1}.

4. Conclusions

Adsorption, thermally induced dehydrogenation, and thermally induced decomposition of methanethiol have been characterized as a function of temperature and coverage on the Pt(111) surface. The species that form on the surface are determined by both temperature and the availability of free Pt sites. Low coverages strongly

favor low temperature dehydrogenation and decomposition reactions. Initial S–H bond activation does not occur at 110 K on crowded surfaces while complete decomposition of methanethiol is observed for 5% of a monolayer on a clean surface. On the other hand, intact methanethiol molecules remain on the (2 × 2)-S pre-sulfided surface up to 180 K. For a saturated monolayer of methanethiol on the clean Pt surface, XPS results indicate that about 60% of the carbon remains on the surface after heating to 750 K indicating that the remaining 40% of the carbon desorbs as CH_4, and C_2H_4. The fractional yield of volatile organic products increases with increasing initial coverage of methanethiol up to monolayer coverage. The structure and geometry of the adsorbed intermediates formed by CH_3SH decomposition also depend on coverage and temperature. Thermal dehydrogenation generates first CH_3S, then CH_2S as previously reported. In addition a new σ-bonded SCH intermediate is identified on a partially covered Pt surface. On the pre-sulfided surface the S–C bonds tend to be oriented more closely along the surface normal than they are on the clean surface.

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