diffusion. The solution to the Smoluchowski equation¹⁸ for 1-D motion is

$$W(x,t|x_0,t_0) = \frac{e^{-(x-x_0)^2/4D_0}}{(2\pi Dt)^{1/2}}$$

and is valid even when D is itself a function of t, i.e., D = D(t).

The mean-square displacement $\langle \Delta x(t)^2 \rangle$ is related to the diffusion processes:

$$\langle \Delta x(t)^2 \rangle = 2D_s t + l^2(1 - f(t))$$

When D_s is the diffusion of the slower process and f(t) is a monotonically decaying function with unit amplitude at t = 0. f(t) has a slowest exponentially decaying component with characteristic time τ . l^2 is related to the length of delocalization:

$$l^2 = \frac{1}{3}L^2$$

Let us approximate f(t) by $e^{-t/\tau}$ where $\tau = l^2/2D_f$. D_f is the diffusion coefficient for the faster process. The diffusion coefficient, D(t), is related to the mean-square displacement by

$$D(t) = \frac{1}{2} \frac{\partial \langle \Delta x(t)^2 \rangle}{\partial t} = D_{\rm s} + D_{\rm f} e^{-t/t}$$

Then at short times $D(t) = D_{\rm S} + D_{\rm f} \simeq D_{\rm f}$, and at long times D(t) $\simeq D_{\rm s}$. Since $D_{\rm f} = D$, as given in the text, $D_{\rm f}$ is not an activated process; $D_{\rm f}$ dominates the diffusion at short times. The temperature dependence of R_1 results from mechanisms which determine D. R_1 depends on $J(\omega)$ terms where ω is the spectrometer frequency, which corresponds to short times, on the order of $1/\omega$.

 $D_{\rm s}$ is the diffusion coefficient for overlall migration of the defect. $D_{\rm s}$ may be associated with a thermally activated process. This process will then contribute through terms which depend on J(0). The ENDOR data and spin-spin dephasing time, $T_{\rm M}$, have J(0)terms which R_1 does not have. Since $1/T_M$ is much larger than R_1 , terms which contain J(0) are important to $1/T_M$ and depend on long-time components of the diffusion.

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Organosulfur Chemistry on W(211) Surfaces. 1. A Comparison of Methanethiol and Methanol

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The reactions of methanol and methanethiol on clean, oxided, sulfided, and carbided W(211) surfaces were studied by LEED, AES, and TPR. Adsorption occurred by an oxidative addition in which the hydroxyl or sulfhydryl hydrogen was removed forming methoxy and methanethioxy intermediates. Clean W(211) was a very strong reductant totally decomposing the molecules. Adsorbed oxygen oxidized the surface making it a weaker reducing agent so that alkoxy and thioxy intermediates were stabilized. An epitaxial surface oxide was a mild oxidant compared to clean W(211); this surface oxidized methanol to formaldehyde. Adsorbed sulfur severely reduced methanol adsorption. Surfaces with adsorbed sulfur adsorbed methanethiol. This adsorption suggests the formation of a disulfide species. Carbided W(211) stabilized both alkoxy and thioxy intermediates as well as oxidizing methanol to formaldehyde. The adsorbed methoxy and methanethioxy intermediates decomposed by C-O or C-S bond scission forming adsorbed methyl groups which either decomposed or were hydrogenated to form methane. At temperatures above 500 K methyl groups recombined and C_2 hydrocarbon products evolved. Surface oxides and carbides oxidized methoxy to formaldehyde and CO, but no surface oxidized methanethioxy to thioformaldehyde or CS.

Introduction

The removal of sulfur from organic sulfur compounds is extremely important in petroleum refining. Oxided and sulfided molybdenum or tungsten catalysts are widely used for hydrodesulfurization.^{1,2} Although extensive studies characterizing the catalyst have been carried out very little work has addressed the organic chemistry at the surface. Zdrazil reviewed the chemistry of typical sulfur impurities in petroleum.³ Of particular significance is the difference in chemical behavior of the sulfur in saturated compounds, such as thiols, to that observed for aromatic compounds such as thiophene. Both aliphatic and aromatic sulfur compounds are found in petroleum; however, sulfur removal from aromatic compounds requires more severe reaction conditions than sulfur removal from aliphatic compounds.

The reaction mechanism of desulfurization has generally been hypothesized to be adsorption at anion vacancies in a WS₂ lattice via the lone electron pair on the sulfur as shown in the following scheme.



Scission of the C-S bond forms a desulfurized product and leaves adsorbed sulfur which is subsequently reduced to H₂S.^{2,4} Desulfurization of thiophenic rings is hypothesized to be similar to other sulfur compounds, though the resonance stabilization makes C-S bond scission more difficult.

In an effort to elucidate the surface chemistry of desulfurization the reactions of sulfur compounds on well-characterized tungsten surfaces have been studied by temperature programmed reaction (TPR), LEED, and Auger electron spectroscopy (AES). This paper reports a comparative study of the reactions of methanethiol and methanol on W(211) surfaces with carbon, oxygen, and sulfur adlayers. As alcohols and thiols are structural analogues this comparison permits us to probe the role of individual substituent atoms. The reaction mechanism for desulfurization given above

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Figure 1. Schematic of the apparatus.

is not sufficient to properly account for the reaction behavior observed. This deficiency becomes more apparent when the reactions of aromatic compounds are considered; the reactions of thiophenic compounds are treated in a subsequent paper.

Experimental Section

The experiments were carried out in an ion pumped stainless steel ultrahigh vacuum system equipped with 4-grid LEED optics, glacing incidence electron gun, quadrupole mass spectrometer, and gas dosing system. A schematic of the system is shown in Figure 1. A 12-mm diameter \times 0.2-mm thick W(211) single crystal (Cornell Materials Research Laboratories) was mounted on a rotatable sample manipulator. The sample could be cooled by conduction through a copper braid which was in contact with a liquid nitrogen reservoir, and heated by radiation from a tungsten filament located 4 mm behind the crystal. Temperatures in excess of 1000 K were achieved by electron bombardment heating. Temperatures were monitored by W-5% Re/W-26% Re thermocouples spotwelded to the W(211) crystal.

The W(211) crystal was cleaned by heating to 1600 K in 10^{-6} torr of oxygen, and subsequently flashing to 2200 K under vacuum. The structure and composition of the surface was verified by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Auger spectroscopy was performed using the LEED optics as a retarding field analyzer. The clean surface showed less than 0.01 monolayer of impurities (1 monolayer = 8×10^{14} cm⁻²). Well-defined adlayers of oxygen, carbon, and sulfur were prepared, and the LEED and AES results were correlated to establish surface coverages.⁶ The AES correlation provides accurate surface coverages to ±0.02 monolayers.

The materials used in these studies were H_2S (Matheson 95%), ethene (Matheson 99.9%), O_2 (Matheson 99.999%), methanethiol (Matheson 98%), and methanol (Fisher Scientific 99.9%). Both the H_2S and CH_3SH decomposed over time and were diluted in H_2 to varying extent; however, this did not cause any difficulties in the studies reported here. Mass spectroscopy was used to check all samples for purity.

Prior to any experiment the crystal was prepared with a prescribed surface composition and structure. In a typical TPR experiment the crystal was cooled to 250 K, and the reactive gases were directed at the crystal surface through a 0.20-mm-i.d. tube. This molecular beam provided high gas fluxes at the surface, while the pressure rise in the vacuum system was kept below 5×10^{-9} torr. A gas manifold was filled with methanol vapor in equilibrium with liquid methanol at 274 K, or methanethiol vapor at approximately 1500 torr. The pressure in the manifold was sub-

TABLE I: Fragmentation Patterns of Reaction Products

species	m/q ratio: relative yield		
H ₂	2:100		
ĊĤ₄	15:100	16:85	14:12
H ₂ O	18:100	17:20	
$\tilde{C_2H_2}$	26:100	25:20	
C ₂ H₄	28:100	27:60	26:60
C_2H_6	28:100	27:30	26:25
co	28:100	16:8	
H ₂ CO	29:100	30:90	28:50
CH₃OH	15:100	31:85	32:60
H,S	34:100	32:40	
CH₃SH	15:100	47:40	

sequently reduced to 250 mtorr. The gas was admitted to the vacuum system by opening an on/off valve. The gas flux into the vacuum system was assumed to be the same as that of carbon monoxide admitted to the vacuum system under identical conditions. The CO flux was determined from the steady-state pressure rise in the vacuum system with CO leaking into the vacuum system from a backing pressure of 250 mtorr. A total beam flux of 3×10^{15} molecules/s was determined. To control the total pressure the valve was opened, and then the crystal was rotated into the path of the beam. After a fixed period of time the crystal was turned away from the beam and the valve was closed. A cosine flux distribution for the effluent from the tube was assumed to estimate the flux at the crystal surface. This is probably a low estimate as a collimated beam is expected. The exposures are estimated to be accurate to within a factor of 3. Sticking probabilities of methanol and methanethiol on clean W(211) at 250 K were found to be near unity.

After adsorption of the reactant, the crystal temperature was ramped at 12 K/s to 800 K, and five temperature programmed mass spectra were recorded simultaneously by a computer. Reaction products were identified by their fragmentation patterns. The fragmentation patterns used are summarized in Table I. Quantitative yields were calculated by using the technique of Ko et at.⁹ Auger spectra were recorded after heating to 800 K and product yields of adsorbed attomic species were determined by AES. Calibration standards for AES are published elsewhere.⁶ The TPR results have been summarized in terms of reaction temperature and product yields.

Well-characterized W(211) surfaces with carbon, oxygen, and sulfur adlayers were prepared by procedures previously described.⁶ A brief account of the preparation techniques and surface structures is given below.

W(211). A clean W(211) surface was prepared by heating the crystal in an effective pressure of 10^{-6} torr of O₂ at 1600 K and then flashing to 2200 K under vacuum. This procedure was repeated until AES indicated surface contamination was negligible (<0.01 monolayer, 1 monolayer (1 ML) = 8×10^{14} cm⁻²). The W(211) surface is a series of raised close-packed rows in an alternating hill-valley structure.

 $W(211)-p(1\times 1)O$. A clean W(211) surface was exposed to ca. 1×10^{15} molecules of O_2/cm^2 and annealed to 1000 K. A (1×1) LEED pattern was obtained and the AES indicated an oxygen coverage of 1 ML; it has been suggested that the oxygen atoms fill in the valleys between the raised rows of tungsten atoms.⁶⁻⁸ After initial characterization by LEED and AES, the oxygen coverage monitored by AES alone was used to verify the starting surface.

 $W(211)-p(1\times 2)O$. A clean W(211) surface was exposed to ca. 2 × 10¹⁵ molecules of O₂/cm² and annealed to 1000 K. A sharp (1 × 2) LEED pattern was obtained with the AES indicating an oxygen coverage of 1.5 ML. This surface is suggested to result from a periodic expansion and compression of the surface, with adsorbed oxygen occupying alternating doubly and singly filled valleys.^{6,7} The p(1×2) pattern persisted over a wide coverage range of oxygen. AES was used to monitor coverage and a value of θ_0

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Figure 2. (A) Representative TPR Data for Methanethiol on W- $(211)-p(1\times 2)O$. (B) Representative AES data for methanethiol on W $(211)-p(1\times 2)O$: (a) before adsorption; (b) after a TPR experiment.

= 1.5 ± 0.1 ML was used in these studies.

 $W(211)-p(1 \times n)O$. High-temperature (>1150 K) exposure of W(211) to O₂ produced (1 × 3), (1 × 4), and (1 × 5) LEED patterns, all with approximately the same oxygen coverage of θ_0 = 1.8 ML. These LEED patterns appear to result from a reconstructed surface oxide.⁶

 $W(211)-c(2 \times 2)S$. An exposure of ca. 10¹⁵ molecules/cm² of H₂S and subsequent heating to 700 K produced a sharp c(2 \times 2) LEED pattern with a sulfur coverage measured by AES of $\theta_{\rm S} = 0.5$. This structure is hypothesized as resulting from sulfur atoms occupying a staggered configuration in the valleys of the W(211) surface.⁶

 $W(211)-c(2\times6)S$. Heating the W(211) surface to 1200 K while exposing it to H₂S produced a c(2×6) LEED pattern with a sulfur coverage of $\theta_{\rm S} = ^{7}/_{6}$ ML. This structure has been proposed to result from sulfur filling $^{2}/_{3}$ of the valley sites in a periodically expanded and contracted surface after the c(2×2) structure is fully developed.⁶

 $W(211)-c(6\times 4)C$. Cracking ethylene over the W(211) surface at 1500 K produced a surface carbide with a $c(6\times 4)$ LEED pattern and a carbon coverage of $\theta_C = 1.3$ ML. This structure has been attributed to the formation of a tungsten carbide overlayer coincident on the underlying tungsten lattice.⁶

Results

The object of the studies reported here was to compare the reaction behavior of methanol and methanethiol on clean, oxided, sulfided, and carbided W(211) surfaces. Temperature programmed reaction (TPR) and Auger electron spectroscopy were used

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 TABLE II: Summary of Methanol Decomposition on W(211)

 Surfaces^a

	reaction	desorpn	:-1.4b
surface	product	temp, K	yield
W(211)	H ₂	340	0.04
		440	0.16
		585	0.08
	CH₄	400-500(b)	0.01
	C(a)		0.46
	O(a)		0.46
$W(211)-p(1 \times 1)O$	H_2	420	0.08
		580	0.04
	CH_4	580	0.08
	СН₃ОН	380	0.04
	C(a)		0.21
	O(a)		0.24
$W(211)-p(1\times 2)O$	H_2	400-600(b)	0.07
	CH₄	580	0.07
		660	0.10
	СН₃ОН	380	0.10
	C(a)		0.04
	O(a)		0.16
$W(211)-p(1 \times n)O$	H_2	400	0.04
		600	0.01
	CH₄	660	0.25
	H ₂ O	660	0.04
	СН₃ОН	380	0.04
	H ₂ CO	660	0.02
	CO	660	0.05
	C(a)		0
	O(a)		0.20
$W(211)-c(2\times 2)S$	H_2	400-550(b)	0.10
	C(a)		0.36
	O(a)		0.37
$W(211)-c(2\times 6)S$	H_2	400500(b)	0.03
	C(a)		0.16
	O(a)		0.17
W(211)-c(6×4)C	H_2	480	0.12
	CĤ₄	480	0.25
	H ₂ O	540	0.04
	CÕ	480	0.02
		700	0.10
		830	0.13
	H ₂ CO	480	0.02
	Сн₃он	380	0.08
	2	480	0.11
	C(a)		-0.18(c)
	O(a)		0)
			-

^a(a) Denotes adsorbed atomic species at 800 K; (b) denotes broad featureless peak; (c) carbon depletion by reaction. ^bMonolayers \pm 0.02. 1 monolayer = 8 × 10¹⁴ cm⁻².

to determine reaction product yields and desorption temperatures. Figure 2 shows a representative set of data for the reaction of methanethiol on a W(211)- $p(1\times 2)O$ surface. The TPR data shown in Figure 2A represent the desorption spectra from a single experiment. A series of two or three such experiments were repeated with a single mass repeated from run to run as a consistency check on the data. The computer acquired desorption rate and temperature data vs. time. The rate data were integrated directly to obtain product yields. From the AES data shown in Figure 2B, the adsorbed product yields were determined from the Auger spectrum taken after adsorption and heating to 800 K. The peak heights for oxygen (O(KLL) at 503 eV), carbon (C(KLL) at 272 eV), and sulfur (S(LMM) at 152 eV) were ratioed against the W(MNN) transition at 350 eV and compared with calibration standards established by LEED-AES correlation to determine surface coverages

In all the experiments a saturation exposure was determined by increasing the exposure until no significant changes were observed in the TPR or AES results when the exposure was increased by an order of magnitude. On all the surfaces examined, both methanol and methanethiol achieved saturation coverages at exposures of less than 10^{16} molecules/cm² for crystal temperatures of 250 K. The results of the reactions of methanol and methanethiol on a series of W(211) surfaces are summarized in Tables

 TABLE III: Summary of Methanethiol Decomposition on W(211)

 Surfaces^a

surface	reaction	desorpn	
(monolayers)	product	temp, K	yield ^b
W(211)	H ₂	350	0.06
		410	0.10
		585	0.03
	CH₄	410	0.32
	C(a)		0.55
	S(a)		0.90
W(211)-p(1×1)O	H_2	400-600(b)	0.15
	CH₄	390	0.29
	C(a)		0.13
	S(a)		0.45
$W(211)-p(1\times 2)O$	H_2	400-600(b)	0.10
	CH₄	390	0.14
		550	0.08
	CH ₃ SH	330	0.04
	C(a)		0.04
	S(a)		0.21
$W(211)-p(1 \times n)O$	H_2	400-550(b)	0.15
	CH ₄	550	0.24
	$C_2H_2^c$	550	0.03
	CH₃SH	330	0.03
	C(a)		0.04
	S(a)		0.35
$W(211) - c(2 \times 2)S$	H_2	400	0.10
	CH ₄	400	0.60
	C(a)		0.20
	S(a)	410	0.80
$w(211) - c(2 \times 6)S$	H ₂	410	0.06
	CH ₄	410	0.48
	C(a)		0.16
	S(a)	250 500(1)	0.60
$W(211) - c(6 \times 4)C$	H_2	350-500(b)	0.14
	CH_4	380	0.25
	CILC	480	0.35
	C_2H_2	480	0.07
	CH3SH	320	0.02
	$\mathcal{O}(z)$	480	0.03
	C(a)		0 0 0 0
	5(a)		0.83

^{*a*}(a), (b), and (c) as in Table II. ^{*b*}Monolayers ± 0.02 . ^{*c*}C₂ hydrocarbon product, assumed to be ethylene.

II and III. Desorption product yields and desorption temperatures are listed, corresponding to a "saturation exposure" at 250 K. Adsorbed atomic product yields, determined by AES, represent the difference between what was present on the surface before adsorption and what was present after the TPR experiment. It should be noted that the material balance closures were good for C and O in the case of methanol and C and S in the case of methanethiol. The material balance closures in the case of hydrogen were always low. This may be attributed to hydrogen desorption occurring at 250 K, during the adsorption process.

Methanol. Table II summarizes the reaction products, desorption temperatures, and product yields for methanol reactions. These results are for exposures of ca. 10^{16} molecules/cm² at 250 K. Higher exposures did not show any changes in surface coverage or reaction paths.

The principal desorption product from an initially clean W(211) surface was hydrogen, which desorbed at 340, 440, and 585 K. A small amount of methane was observed to evolve between 400 and 500 K. H₂ recombination on clean W(211) occurred at 330 and 600 K,¹⁰ suggesting that the evolution of H₂ from methanol decomposition was in part due to recombination of adsorbed hydrogen. Hydrogen desorption at 440 K and the evolution of methane suggests the decomposition of a surface intermediate as has been observed on other tungsten surfaces.⁹⁻¹¹ In separate experiments no methane evolved while heating either W(211)–



Figure 3. Product yields as a function of exposure from methanol adsorption on W(211).

c(6×4)C or W(211)-c(2×4))CO(β) surfaces in the presence of a hydrogen flux at the crystal surface. In addition, AES detected adsorbed carbon and oxygen reaction products. The ratio of adsorbed carbon to oxygen was 1.0, in agreement with the TPR results indicating the methane yield was <1 × 10¹³ molecules/cm². The adsorbed carbon and oxygen recombined and desorbed as CO at 1000 and 1200 K.

Exposure of the W(211) surface to less than 10¹⁵ molecules/cm² of methanol reduced the H₂ product yield at 440 K, and the methane yield decreased below the limit of detectability. The only reaction products detected were H₂ and adsorbed carbon and oxygen. The C/O ratio of the adsorbed products was unity, and the product yields of adsorbed carbon and oxygen increased in a linear fashion with methanol exposure, as shown in Figure 3. The results shown in Figure 3 indicate excess hydrogen desorption at low methanol coverages. This results from hydrogen adsorption from the background prior to the TPR experiment. Figure 3 also indicates that hydrogen formed from methanol decomposition is displaced from the surface at methanol exposures greater than 2×10^{14} molecules/cm². For higher exposures there was a deficiency of hydrogen among the reaction products. This was consistent with the observation that hydrogen adsorption was suppressed on surfaces with adsorbed carbon and oxygen.^{6,12,13} The results presented in Figure 3 show that clean W(211) effecively decomposed methanol to adsorbed atomic constituents up to the point where the surface was saturated with adsorbed carbon and oxygen. A surface saturated with carbon and oxygen was not active for further methanol adsorption at 250 K.

Oxygen adlayers led to the stabilization of molecular intermediates on the tungsten surface. On a W(211)- $p(1\times1)O$ surface methanol desorbed molecularly at 380 K, similar to the result obtained for W(100).¹⁴ The methane product yield increased relative to the clean surface, and the methane product desorbed at 580 K. Adsorbed carbon and oxygen were observed as reaction products by AES. Hydrogen desorption decreased relative to the clean surface due to the lower surface reactivity, and occurred at 420 and 580 K.

The reactivity of the surface decreased with further adsorption of oxygen. Adsorption of methanol on a W(211)-p(1×2)O surface resulted in increased methanol desorption at 380 K. The methane product increased relative to the W(211)-p(1×1)O surface, and evolved at significantly greater temperatures of ca. 580 and 660 K. This suggested a more stable intermediate on the W(211)p(1×2)O surface. Hydrogen desorption occurred in a rather broad

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Figure 4. Methanol adsorption at 250 K and methane product yield from methanol reaction on oxidized W(211).

featureless peak. Adsorbed oxyben was observed as a reaction product but very little adsorbed carbon was observed as a reaction product.

A reconstructed surface oxide, the W(211)- $p(1 \times n)O$ surface displayed slightly more complex chemistry. Similar to the surfaces with adsorbed oxygen, adsorbed methanol desorbed at 380 K from the reconstructed surface. Methane evolved by reaction on the reconstructed surface at 660 K. The distinguishing feature on the reconstructed oxide was the coincident evolution of H₂CO, H₂O, and CO with CH₄ at 660 K. Adsorbed oxygen was a reaction product balancing the CH₄ yield.

Figure 4 summarizes the chemical activity of the oxidized W(211) surfaces for methanol adsorption and methane formation from methanol. Methanol adsorption was measured from a carbon and/or oxygen balance for all reaction and desorption products after an exposure of ca. 10^{16} molecules/cm² at 250 K. The results in Figure 4 show that as the adsorbed coverage increased up to $\theta_0 = 1.5$ mL, methanol adsorption decreased while the methane yield increased, indicating increased stability of molecular intermediates. Both adsorption of methanol and methane formation increase for $\theta_0 = 1.8$; this appears to be the result of surface reconstruction for the W(211)-p(1×n)O surface and will be discussed below.

Adsorbed sulfur on W(211) reduced adsorption and reaction of methanol with the surface. Any methanol that adsorbed on the sulfided surfaces totally decomposed. Hydrogen along with adsorbed carbon and oxygen were the only reaction products from methanol adsorption on sulfided W(211). Figure 5 shows the reduced extent of adsorption and reactivity of methanol on sulfided W(211). Methanol adsorption at 250 K and methanol reactivity, as indicated by oxygen adsorption and methane production, both decreased with sulfur coverage; no methanol adsorption was detected for sulfur coverages above 1.5 ML.

Carburization of W(211) produced a ditungsten carbide-like overlayer⁶ that stabilized methoxy intermediates and led to high methane yields from methanol decomposition. The reaction products and reaction temperatures were similar to those seen for methanol reacting on a W(100)-(5×1)C surface.⁹

Methanethiol. Table III summarizes the TPR results for methanethiol on W(211) surfaces. These results are for exposures of 10^{16} molecules/cm² at 250 K.

Figure 6 shows the reaction product yields from methanethiol as a function of exposure. For exposures less than 6×10^{14} molecules/cm², the only reaction products observed were H₂ and adsorbed carbon and sulfur. The hydrogen desorbed at 350 and 580 K by what appeared to be desorption-limited processes. The adsorbed carbon and sulfur recombined and desorbed as CS at 1450 K. For exposures greater than 6×10^{14} molecules/cm², a



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Figure 5. Methanol adsorption at 250 K and methane product yield for methanol reaction on sulfided W(211).



Figure 6. Product yields as a function of exposure from methanethiol adsorption on W(211).

molecular intermediate stabilized on the surface. This intermediate reacted to yield methane and hydrogen at 410 K, and adsorbed sulfur. For methanethiol exposures between 6×10^{14} and 3×10^{15} molecules/cm² there was an increase in the yields of methane and adsorbed sulfur, and only a minor increase in the amount of adsorbed carbon. The results shown in Figure 6 indicate a hydrogen efficiency in the reaction products at exposures greater than 2×10^{14} molecules/cm². This is apparently due to hydrogen desorption at 250 K from the surface with adsorbed carbon and sulfur. No sulfur-containing desorption products were detected during the TPR experiments below 1000 K.

Figure 3 shows that methanol adsorption was inhibited on W(211) after saturating the surface with adsorbed carbon and oxygen. However, methanethiol readily adsorbed on a W(211) surface even after it was saturated with carbon and sulfur, leading to a stabilized molecular intermediate. In two related experiments, methanol showed negligible adsorption on a surface covered with adsorbed carbon and sulfur where $\theta_S = \theta_C = 0.45$ ML, and methanethiol would not adsorb on a surface with adsorbed carbon and oxygen where $\theta_C = \theta_0 = 0.45$ ML. These results suggest a fundamental difference in the adsorption of alcohols and thiols, as discussed below.

Oxygen adlayers on W(211) inhibited methanethiol decomposition and stabilized molecular intermediates, analogous to the results for methanol. A small amount of methanethiol desorbed



Figure 7. Methanethiol adsorption at 250 K and methane product yield from methanethiol reaction on oxidized W(211).

from a W(211)-p(1×1)O surface at 320 K. Methane evolved at 390 K. The sulfur accumulation was approximately half that observed on clean W(211), and the methane yield approximately equalled the sulfur accumulation. Hydrogen desorbed in a broad peak between 400 and 600 K. Further adsorption of oxygen appeared to block adsorption sites for methanethiol adsorption. On the W(211)-p(1×2)O surface the methane yield and sulfur accumulation were half of those observed for W(211)-p(1×1)O. Methane desorbed at 390 K, suggesting a similar reaction on both the p(1×1)O and p(1×2)O surfaces. In addition, a new methane product peak was observed at 550 K. Desorption of hydrogen from CH₃SH decomposition on W(211)-p(1×2)O occurred in a broad featureless peak. The desorption of molecularly adsorbed CH₃SH from W(211)-p(1×2)O occurred at 330 K.

On the W(211)-p($1 \times n$)O surface the methanethiol adsorption resulted in a small amount of CH₃SH desorption at 330 K. Methane and a C₂ hydrocarbon desorbed coincidentally at 550 K. The C₂ hydrocarbon was identified by an m/q 26 fragment; however, the product yield was too low to unambigouosly identify the fragmentation pattern. Other than methanethiol, no sulfurcontaining products were observed to desorb below 1000 K from any of the oxided surfaces. The adsorbed sulfur desorbed as atomic sulfur at 1850 K, and as SO at 1780 K.

Figure 7 summarizes the results for methanethiol adsorption and reactivity on oxidized W(211). The results show decreased adsorption with oxygen coverage up to $\theta_0 = 1.5$ ML, but adsorption did increase for the reconstructed oxide surface. The methane yield from methanethiol showed a slight decrease with oxygen coverage up to $\theta_0 = 1.5$ ML, the opposite trend observed from the methanol reaction. However, the methane yield increased for the reconstructed oxide.

In contrast to methanol, methanethiol showed significant adsorption and reaction on sulfided W(211). Figure 8 indicates that the adsorption of methanethiol, as measured by CH₃SH desorption plus CH₄ product yield, remained high on W(211) with adsorbed sulfur. In addition, the methane product yield increased initially followed by a slight decrease with sulfur coverage. The surface coverage of sulfur did not affect the energetics of the methanethiol decomposition to methane, as indicated by rather minor shifts in the CH₄ TPR peak temperature. As observed on the other W(211) surfaces, no sulfur-containing reaction products other than methanethiol were observed below 1000 K; only CS and S were observed to desorb at 1450 and 1850 K, respectively.

On the carbided W(211) surface methanethiol readily adsorbed and reacted. Methanethiol desorbed at 320 and 480 K. The lower temperature desorption was probably due to molecularly adsorbed CH₃SH. The desorption at 480 K coincided with the evolution of CH₄ and a C₂ hydrocarbon, suggesting the decomposition of



Figure 8. Methanethiol adsorption at 250 K and methane product yield for methanethiol reaction on sulfided W(211).

a molecular intermediate which also reacted with adsorbed hydrogen to give CH_3SH . The methane yield from the carbided surface was greater than that observed from any other surface. AES indicated the sulfur residue left on the surface was consistent with the methane yield from this surface.

Discussion

Thiols and alcohols are structurally similar. The differences in reaction behavior indicate the roles of individual substituent atoms. The results obtained here by TPR suggest that methanol and methanethiol form analogous surface intermediates and react by similar reaction pathways. However, the substituent atom can also open up new reaction channels. Differences in reaction pathways appear to be related to differences in bonding of the oxygen and sulfur atoms.

Methanol. The reactions of methanol have been thoroughly studied on clean, carbided, oxided, and sulfided W(100) surfaces.^{9,14} These studies concluded that methanol totally decomposed on clean W(100). Oxygen and sulfur adlayers rendered the W(100) surface inactive for reaction of methanol. A carbided W(100) surface partially oxidized methanol to formaldehyde and carbon monoxide, and partially reduced methanol to methane.

The results presented here show that clean W(211) also totally decomposed methanol to adsorbed atomic constituents. Sulfur adlayers rendered the W(211) surface inactive for methanol decomposition. A carbide adlayer on W(211) was active for partial oxidation, giving rise to the same spectrum of products seen on carbided W(100). In contrast to the results for W(100), oxided W(211) surfaces were active for reduction of methanol to methane. This greater activity on oxided W(211) appears to result from lower coordination of the metal atoms on the W(211) surface. The differences between W(211) and W(100) surfaces will be addressed in a separate note.¹⁵

Previous studies of methanol reactions on W(100) surfaces with carbon and mixed oxygen and carbon adlayers concluded that methanol adsorbed on these passivated surfaces and formed a methoxy intermediate by loss of the hydroxyl hydrogen. The methoxy reacted by both C-O and C-H bond scission to yield primarily CH₄ and CO, with lesser amounts of H₂CO. The results presented here indicated that methanol reacts on W(211) by a similar reaction pathway. A methoxy intermediate was stabilized on oxided and carbided surfaces, and subsequently reacted by C-O bond scission leading to the formation of methane and adsorbed oxygen. The TPR results for methanol on W(211) with oxygen adlayers could also be explained by the existence of adsorbed methyl as the stable surface intermediate. However, methyl

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intermediates are not consistent with the results for the W-(211)- $p(1 \times n)O$ surface where formaldehyde and CO were formed by the same reaction channel as methane.

A useful comparison of the reactivity of the various tungsten surfaces is in terms of oxidation activity. A clean tungsten surface can be viewed as a very strong reducing agent that completely decomposed methanol to form a metal oxy-carbide. By partially oxidizing the surface with carbon or oxygen the reduction potential of the surface is reduced and the methoxy intermediate is stabilized. The loss of the hydroxyl hydrogen from methanol to form a methoxy can be viewed as a redox reaction in which the surface transfers electrons to the oxygen of the adsorbed methanol. Further oxidation would result in more electron transfer from the surface to the adsorbed methoxy, weakening bonds and causing decomposition. Following this line of reasoning, the activity of the surface for decomposing the methoxy should be directly related to the reducing potential of the surface. The temperature at which the methoxy decomposes is indicative of its stability and hence the surface's activity. The following ordering of reduction potential can be established from the data in the Table II.

$$W(211) > W(211)-c(6 \times 4)C > W(211)-p(1 \times 1)O > W(211)-p(1 \times 2)O > W(211)-p(1 \times n)O$$

This ordering suggests that the more severely a surface has been oxidized the weaker its reduction potential. The sulfided tungsten surfaces do not fit into this sequence as sulfur adlayers tend to block adsorption and do not seem to influence the stability of the methoxy intermediate.

One more point should be made concerning the methoxy decomposition on the various oxide surfaces. LEED, AES, and CO adsorption results suggested that the W(211)-p($1 \times n$)O surface was reconstructed such that there was a periodic expansion and contraction of the surface pushing the raised rows of tungsten apart to accommodate oxygen adsorption.⁶ The W(211)- $p(1\times 2)O$ surface was only slightly distorted and the $W(211)-p(1\times 1)O$ surface was unperturbed.⁶ The results for methoxy decomposition support this idea. The W(211)-p(1×1)O surface was the most active oxide surface for methoxy decomposition, as evidenced by the lowest reaction temperature, and showed a single reaction pathway. The W(211)-p(1×n)O surface was least active and again only showed a single reaction pathway. The W(211)-p- $(1\times 2)O$ surface decomposed the methoxy along both reaction pathways observed on the surfaces of lower and higher oxidation potential.

A surprising result is that both the W(211)-p(1×n)O and $W(211)-c(6\times 4)C$ surfaces were active for oxidative adsorption of methanol, whereas the surface with a mixed oxygen carbon adlayer did not adsorb methanol. This result may be due to the nature of the adlayer structures. In both the w(211)-p(1×n)O and W(211)-c(6×4)C structures it was suggested that a surface reconstruction occurred that resulted in metal atoms being exposed at the surface.⁶ This surface reconstruction does not appear to occur for either the W(211)-p(1 \times 1)O surface or the mixed carbon oxygen adlayer. On these surfaces the adatoms block the surface metal atoms and hinder the oxidative adsorption of methanol.

Methanethiol. The interaction of methanethiol with W(211)surfaces parallels the behavior of methanol, but also exhibits some very significant differences. Figure 6 shows that initially clean W(211) reduces CH₃SH to adsorbed atomic constituents. However, in contrast to the behavior observed for methanol, where the surface became inactive for methanol adsorption after a mixed monolayer of oxygen and carbon were adsorbed, methanethiol, adsorbed on a surface with a mixed sulfur and carbon monolayer and subsequently reacted to form methane. This same difference in reaction behavior between methanol and methanethiol was also observed on W(211) with sulfur adlayers. The adsorbed sulfur inhibited methanol adsorption. Methanethiol was observed to adsorb on sulfided W(211) surfaces, and methane was observed as the reaction product.

The difference in reaction behavior of the alcohol and thiol may be accounted for by the oxidative adsorption process previously hypothesized for methanol adsorption. Methoxy formation was

hypothesized to occur by the oxidation of methanol by the surface. as shown in the reaction.

$$CH_3OH + W \rightarrow CH_3O^-W^+ + H(a)$$

Thiols are known to be oxidized to disulfides under mild oxidation conditions.^{16,17} If the surface acts as an oxidant, methanethiol may be adsorbed by oxidation to form a disulfide with the surface as shown in following reaction.



The alcohol and thiol are suggested to form analogous alkoxy and thioxy intermediates. However, the substituent atom would play the important role of modifying the reaction pathways as the thiol may be oxidized to a disulfide species. It is important to note that peroxy and sulfoxy bonds are not formed under mild oxidation conditions and so this type of reaction would not be expected with alcohols.

On oxided tungsten surfaces the reactions of the alcohol and the thiol show almost identical behavior. The W(211)-p(1×1)O surface stabilized intermediates from both methanol and methanethiol adsorption which decomposed to give methane. The $W(211)-p(1 \times n)O$ surface also stabilized the same intermediates, but this surface was less active for reduction, and the intermediates decomposed at higher temperatures. The W(211)-p(1 \times 2)O surface showed a combination of the activity of the other two oxide surfaces for both methanol and methanethiol. These results suggest that the methanol was partially oxidized to a methoxy intermediate and methanethiol was oxidized to a methanethioxy intermediate. The results mitigate against a methyl type of intermediates. A methyl species from methanol and methanethiol should react at similar temperatures. However, methane evolution from methanol and methanethiol occurred at distinctly different temperatures suggesting different intermediates. The C-S bond in methanethioxy is weaker than the C-O bond in methoxy, and hence the thioxy should react at a lower temperature. In all cases methane evolution from methanethioxy was seen at significantly lower temperatures (nearly 100 K) than methane from methoxy.

The results for methanethiol reacting on $W(211)-c(6\times 4)C$ indicated that methane evolved in two reaction steps, in contrast to the reaction of methanol where a single reaction event produced methane. The TPR and AES data do not suggest any clear difference between the two systems to indicate what caused the dissimilar results. Two possibilities are formation of a dimethyl disulfide species on the surface, or possibly the formation of dimethyl sulfide and adsorbed sulfur. The adsorbed sulfur could then react with another methanethiol and produce methyl disulfide adsorbed to the surface. Other possibilities exist and further work needs to be done to clarify the two reaction pathways.

A Mechanistic Comparison of Methanol and Methanethiol. The TPR results cannot unequivocally establish the existence of either the methoxy or methanethioxy intermediate, and more work needs to be done to firmly establish their existence. However, the reaction products and the known chemistry of alcohols on transition-metal surfaces support this hypothesis. The formation of stable alkoxys on transition-metal surfaces is well established.¹⁸⁻²⁰ Thioxys have also been hypothesized by a number of previous investigators.²¹⁻³¹ The surprising new result is the

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TABLE IV: Heats of Reaction for Adsorption on Tungsten Surfaces

reaction	ΔH , kcal/mo
$W(s) + CH_3OH(g) \rightarrow C(a) + O(a) + 4H(a)$	-89
$W(s) + CH_3SH(g) \rightarrow C(a) + S(a) + 4H(a)$	-87
$W(s) + CH_3OH(g) \rightarrow CH_3O-W + H(a)$	-27
$W(s) + CH_3SH(g) \rightarrow CH_3S-W + H(a)$	-15
$W = O(s) + CH_3OH(g) \rightarrow W - O - OCH_3 + H(a)$	+64
$W = O(s) + CH_3SH(g) \rightarrow W - O - SCH_3 + H(a)$	+26
$W = S(s) + CH_3OH(g) \rightarrow W - S - OCH_3 + H(a)$	+13
$W = S(s) + CH_3SH(g) \rightarrow W - S - SCH_3 + H(a)$	-11

suggestion that a thiol can adsorb by disulfide formation. This reaction could be driven by the strong S-S bonds that form in disulfides relative to weaker W-S bonds that would be disrupted in disulfide formation. Peroxy and sulfoxy bonds are weaker than W-O bonds so that alcohol adsorption is inhibited on sulfided and oxided surfaces. A quantitative comparison of the reaction paths can be made by comparing the enthalpies for the various possible reactions following the method suggested by Benziger and Madix.32 Table IV lists the heats of reaction for the various reaction pathways. The Appendix provides the details of how these numbers were determined. Based on these estimates, reactions should be considered feasible only if the enthalpy is exothermic, as all are accompanied by a large loss of entropy in the adsorption step. The results in Table IV indicate that the only feasible reactions are total decomposition of methanol and methanethiol on the clean tungsten surface, the formation of methoxy and methanethioxy intermediates bound directly to surface metal atoms, and the adsorption of methanethiol on a sulfided surface by disulfide formation.

The thermodynamic driving forces agree with the observed reaction behavior. The findings suggest that clean tungsten surfaces reduce both the alcohol and the thiol to adsorbed atomic constituents. Methoxy and methanethioxy intermediates form on the oxide surfaces, with bonds formed directly between the surface metal atoms and the oxygen in the methoxy or the sulfur in the methanethioxy. Adsorbed sulfur blocks methanol adsorption on sulfided surfaces, and methanol adsorption only occurs at places where the metal atoms are exposed. Where the metal surface is exposed complete reduction to adsorbed constituents occurs. Methanethiol adsorbs on sulfided tungsten surfaces by formation of a disulfide intermediate. The disulfide can also form on initially clean surfaces that are sulfided by the decomposition of methanethiol.

Based on the redox chemistry proposed here for alcohol and thiol adsorption, the inhibition of alcohol adsorption on the sulfided surfaces was unexpected. The data suggest that adsorbed sulfur sterically hinders methanol adsorption. For equivalent surface coverages of oxygen and sulfur, the sulfur more severely poisons methanol adsorption. In terms of electronic structure oxides are more ionic than sulfides, so any electronic effect on adsorption is expected to be greater for oxided surfaces. The observation of the opposite effect for methanol adsorption suggests that sulfur effectively blocks the metal surface. This had previously been proposed for methanol adsorption on W(100),¹⁴ and CO adsorption on Fe(100).³³

The idea of a redox reaction has been extended to surfaces here to account for the surface chemistry. This is a natural extension of concepts used to account for oxidation catalysis on metal oxide catalysts.^{34,35} The results show that oxidation of the surface reduces its reduction potential for reduction of an alcohol or a thiol. The effect of sulfur adlayers on methanol adsorption suggest

TABLE V: Enthalpies of Formation and Adsorption

$\Delta H_{\rm f}$, kcal/mol	ref	
-5.5	36	
-5.7	36	
+32.5	36	
-48	36	
-30	36	
+3.5	36	
+1.5	36	
+53.2	38	
+59.6	38	
-136	38	
-46.3	38	
-9	38	
-30	6	
	$ \Delta H_{\rm f}, \ \mbox{kcal/mol} \ -5.5 \ -5.7 \ +32.5 \ -48 \ -30 \ +3.5 \ +1.5 \ +53.2 \ +59.6 \ -136 \ -46.3 \ -9 \ -30 \ -30 \ \ \ -30 \ \ -30 \ \ -30 \ \ -30 \ \ -30 \ \ -30 \ \ -30 \ \ -30 \ \ -30 \ \ \ -30 \ \ -30 \ \ -30 \ \ \ -30 \ \ -30 \ \ -30 \ \ -30 \ \ -30 \ \ -30 \ \ \ \ -30 \ \ \ -30 \ \ \ -30 \ \ -30 \ \ -30 \ \ \ \ \ -30 \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

that the reaction is also affected by steric effects at the surface. Additional work is needed to provide a more detailed model of this oxidation concept, and to test its validity more rigorously.

Conclusions

The reactions of methanol and methanethiol on W(211) surfaces that have been suggested here are analogous to classical organic reactions of alcohols and thiols reported in standard textbooks.^{1,16} Initial adsorption appears to be due to an electrophilic interaction involving the lone pair electrons on the oxygen or sulfur. Subsequently the hydroxyl or sulfhydryl hydrogen is exchanged for a bond to the surface. The formation of alkoxy and thioxy intermediates are the result of this oxidative adsorption step. The surface can also be modified to alter its oxidizing strength. Clean W(211) is a very strong reducing agent and completely breaks the molecule down to adsorbed atomic constituents. Adsorbed oxygen reduces the reduction strength of the surface and stabilizes methoxy and methanethioxy intermediates. A reconstructed surface oxide is less strongly reducing than adsorbed oxygen, and the methoxy and methanethioxy intermediates react at higher temperatures on the reconstructed surface. Adsorbed sulfur blocked the adsorption of methanol. However, methanethiol adsorbs on sulfided W(211) and appears to form a disulfide surface intermediate. A reconstructed carbide surface possesses intermediate reducing strength to clean and oxide W(211) surfaces.

The adsorbed methoxy and methanethioxy and intermediates react in similar fashion, primarily by C-O or C-S bond scission to form methyl groups which either decompose or are hydrogenated to form methane. The methoxy also reacts by C-H bond scission to form formaldehyde and CO. These reactions are all consistent with dehydration reactions observed for alcohols and thiols in homogeneous systems.

Appendix

Thermochemistry provides a useful and easily applied method to compare the thermodynamic driving forces of chemical reactions. Although the technique is empirical and the approximations are somewhat crude, the results from these calculations are good indicators for thermodynamic feasibility of reaction pathways. These techniques have been extremely useful in examining reaction mechanisms and kinetics of gas-phase reactions.³⁶ Recent extensions to surface reactions were useful in explaining different reaction pathways observed by TPR on different transition-metal surfaces.32,37

In order to understand the differences in chemical reactivity of methanol and methanethiol on clean, oxided, and sulfided tungsten surfaces heats of reaction have been estimated by bond additivity. The following assumptions have been made to estimate bond energies:

(i) Carbon forms four bonds, oxygen and sulfur form two bonds, and hydrogen forms one bond.

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TABLE VI: Enthalpies of Formation of Adsorbed Species

-		
species	$\Delta H_{\rm f}$, kcal/mol	
 W-OCH ₃	-60	
W-SCH ₃	-5.5	
W-O-O-CH3	-37	
W-O-S-CH ₃	-32	
W-S-O-CH ₃	-43	
W-S-S-CH ₃	-24	

(ii) Metal-adatom bonds were estimated from heats of formation of bulk compounds;

$$D(M-A) = \frac{1}{nx} [-\Delta H_{f}(MA_{x})] + \frac{1}{n} \Delta H_{f}(A(g))$$

where n is the number of bonds an adatom forms, as specified in (i).

(iii) The disulfide bond energy was estimated to be the same as in dimethyl disulfide.

(iv) The peroxide bond energy was estimated to be the same as in dimethyl peroxide.

(v) The bond energy of sulfur oxygen single bonds was estimated as half the bond energy of SO.

(vi) Heats of formation of M-A-B-CH₃ were estimated as $\Delta H_{\rm f}({\rm M}-{\rm A}-{\rm B}-{\rm C}{\rm H}_3) =$

 $\Delta H_{\rm f}({\rm MA}) + \Delta H_{\rm f}(\cdot {\rm BCH}_3) + {\rm D}({\rm A-B}) - {\rm D}({\rm M-A})$

Table V lists the thermochemical data used in those calculations. Table VI lists the estimated heats of formation of adsorbed surface intermediates. These estimates were used to compare the enthalpies of reaction for a variety of reactions. Entropies of reaction have been neglected. In all cases the entropy of adsorption is negative so that the free energy will be greater than the enthalpy. Based on these estimates reactions may be assumed to be favorable if the enthalpy is strongly exothermic and unfavorable if the enthalpy is strongly endothermic. Any adsorbed hydrogen was assumed to be adsorbed to the metal. The calculations can be modified to reflect formation of OH or SH groups. In all cases this modification resulted in a negligible difference in the enthalpies of reaction.

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Organosulfur Chemistry on W(211) Surfaces. 2. A Comparison of Benzene, Thiophene, and Tetrahydrothiophene

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The interactions of benzene, thiophene, and tetrahdyrothiophene with clean, oxidized, and sulfided W(211) surfaces were studied with LEED, AES, and temperature programmed reaction. Benzene and thiophene appear to absorb as bases making π -bonds to the surface. Benzene decomposed to yield adsorbed carbon and hydrogen. Thiophene appeared to undergo electrophilic attack at the 2-position forming a carbon bound surface intermediate. This surface intermediate was desulfurized and the resulting hydrocarbon surface intermediate underwent C-C bond scission forming C3 hydrocarbons as the dominate desorption product. The electrophilic attack at the 2-position was shown by methyl group elimination from 2,5-dimethylthiophene. Adsorbed oxygen and sulfur enhanced the adsorption of benzene and thiophene by making the surface more acidic. Tetrahydrothiophene (THT) appear to adsorb as a base, forming a bond between the S(3p) electrons and the surface. Desulfurization of adsorbed THT led to C₄ hydrocarbons as the dominate desorption product. Adsorbed oxygen and sulfur inhibited reaction of THT. These results suggest that the surface reactivity and subsequent desulfurization of thiophene is controlled by electrophilic attack on the aromatic ring, and the ensuing reduction of resonance stabilization facilitates sulfur removal.

Introduction

Desulfurization of thiophene and its derivatives has been extensively studied in an effort to improve hydrotreating catalysts (see reviews in ref 1-4). Thiophene is used as a model compound in many studies as desulfurization of aromatic heterocycles is the most important and most difficult of the desulfurization reactions. Mechanisms of thiophene desulfurization have been proposed by several investigators, but it remains a controversial subject. It is generally assumed that the reaction occurs at anion vacancies in a metal sulfide lattice, or on a bare metal surface.^{5,6} However, conflicting hypotheses have been suggested for the bonding to the surface and the intermediate involved in C-S bond scission.

Schuit and Lipsch⁷ originally proposed that the thiophene ring adsorbed on the surface through the sulfur atom and hydrogenation was accompanied by C-S bond scission to give butadiene and adsorbed sulfur. More recent proposals have suggested partial hydrogenation procedes the C-S bond scission so that the aromatic

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character of the molecule was destroyed.^{9,10} The catalyst had to be bifunctional as it had to hydrogenate the thiophene ring and subsequently desulfurize the sulfide. More recently Kwart et al.8 modified this scheme by suggesting that thiophene adsorbs by formation of a carbon-surface bond, rather than a sulfur-surface bond. Variations on this basic mechanism have been proposed by a number of investigators.⁸⁻¹¹

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