

Controlling Deoxygenation Selectivity by Surface Modification: Reactions of Ethanol on Oxygen- and Sulfur-Covered Mo(110)

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Abstract: The selectivity for ethylene production from the reactions of ethanol on oxygen-covered and sulfur-covered Mo(110) is significantly increased from that on the clean surface. The presence of these surface modifiers inhibits the activity for nonselective decomposition, favoring ethylene elimination. On both the oxygen and sulfur overlayers, ethoxide decomposition yields ethylene and H₂ as the major gaseous products. Water is also evolved on the oxygen-covered surface. The total amount of ethanol decomposition is significantly reduced when sulfur is present such that on the 0.5 ML sulfur overlayer it is only 9% of that on clean Mo(110). The decrease in the total amount of decomposition due to sulfur is attributed to site blocking by sulfur binding in high coordination sites. Surprisingly, oxygen bound to high coordination sites does not significantly inhibit irreversible ethanol reaction until more than half of the sites are occupied. The total amount of ethanol that irreversibly reacts remains nearly constant up to oxygen coverages of 0.5 ML. We propose that the sustained reactivity of the oxygen overlayers is due to the small diameter of oxygen relative to S, so that high coordination sites adjacent to those occupied by oxygen are available for ethoxide coordination. The formation of chemisorbed OH from hydrogen transfer to chemisorbed oxygen on Mo(110) may also play a role in reducing site blocking by oxygen, because the charge and diameter of OH will be smaller than for oxygen itself and because adsorbed OH may move to a slightly different coordination site. On more highly oxidized surfaces, where subsurface and terminal sites (Mo=O) are populated, the amount of ethanol decomposition is significantly reduced. In particular, we show that the Mo=O species does *not* promote ethanol reaction. We attribute the lack of ethanol decomposition on the more highly oxidized surfaces to the lack of facility for OH and water formation and to the absence of vacant coordination sites for the ethoxide. The reactivity of the oxidized Mo(110) is contrasted to MoO₃ catalysts and differences are ascribed to the different oxidation states of the materials.

Introduction

Molybdenum oxides have attracted attention as both industrial oxidation and deoxygenation catalysts. Specifically, molybdenum-based materials are used in the removal of oxygen from fossil fuels.¹ Furthermore, materials such as MoO₃ have been employed as partial oxidation catalysts for the direct conversion of methane to formaldehyde.^{2–9} The oxidation of ethanol to acetaldehyde has also been carried out over MoO₃.^{10–13} In partial oxidation chemistry, oxygen bound at terminal sites has

been proposed as the reactive species,^{3,6,10–13} but the nature of the active sites remains a topic of controversy.^{14–17}

In this study, we have investigated the reactivity of ethanol on well-defined oxygen overlayers in order to test for electronic and geometric modification of the surface reactivity. Specific oxygen coordination sites can be populated by using different exposure conditions.^{18,19} At low coverages (~0.25 ML), oxygen resides in the long-bridge site, based on the observation of a single vibrational mode at ~510 cm⁻¹, which is consistent with C_{2v} symmetry. At higher coverages, oxygen exposures up to saturation at 100 K result in population of low-symmetry, high-coordination sites, as signified by the appearance of both ν -(Mo–O) and δ (Mo–O) below 630 cm⁻¹.¹⁸ The presence of both the stretching and bending modes indicates that oxygen cannot reside solely in the long-bridge sites because only one mode is allowed for C_{2v} symmetry. The oxygen most likely migrates toward the quasi-3-fold sites leading to C_s symmetry,

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in analogy to the known structure of sulfur on Mo(110).²⁰ The peak at $\sim 510\text{ cm}^{-1}$ is also resolved at the higher coverages, indicating that the long-bridge sites are also partially populated at the higher coverages. In addition, overlayers containing both subsurface and terminal oxygen (Mo=O) moieties can be prepared by exposing the surface to O₂ at 1200 K. Although the terminal sites could not be populated in the absence of subsurface oxygen, these overlayers provide a means of investigating the chemical activity of the Mo=O species.

Ethanol chemistry on ordered sulfur overlayers (0.25–0.5 ML) was also studied in order to help distinguish between site blocking and electronic effects, given that sulfur is a larger but less electronegative atom than oxygen. Tensor LEED calculations for S-p(2 × 2)-Mo(110) ($\theta_s = 0.25\text{ ML}$) have shown that sulfur is located closer to the quasi-3-fold site than to the long bridge site.²⁰ Furthermore, electron energy loss data for the 0.4 ML sulfur overlayer also demonstrate that sulfur is not bound at the long bridge site; two modes are observed in the electron energy loss spectrum of the sulfur overlayer, suggesting that sulfur is located near the quasi-3-fold sites.

Herein we report that the selectivity for ethylene production from ethanol over nonselective decomposition increases as a function of oxygen coverage, without a significant decrease in the total amount of irreversible reaction up to oxygen coverages of 0.50 ML. On the other hand, the total reactivity decreases monotonically as a function of sulfur coverage, approaching zero at 0.5 ML. These results indicate that sulfur blocks reaction. Site blocking by sulfur is consistent with the assumption that the reactive intermediate, ethoxide, adsorbs at the quasi-3-fold sites; theoretical studies of methoxide on Mo(110)²¹ and other transition metal surfaces^{22,23} indicate that methoxide prefers to bind at the highest coordination site. The sustained decomposition of ethanol at high oxygen coverages is attributed to the small diameter of oxygen relative to the Mo lattice spacing, while the increased selectivity for ethylene production is most likely related to electronic modification of the Mo atoms in the surface.

Experimental Section

All experiments were performed in an ultrahigh vacuum chamber, which has been described previously, with a base pressure of $< 1 \times 10^{-10}$ Torr.^{24,25} The chamber is equipped with a UTI quadrupole mass spectrometer, electron energy loss analyzer (LK2000), low energy electron diffraction optics, and a cylindrical mirror analyzer (Physical Electronics, model 15-155) for Auger electron spectroscopy. The crystal was biased to -100 V during temperature programmed reaction experiments to prevent electron-induced chemistry. Auger spectra were collected with use of a beam energy of 2.5 keV. Electron energy loss data were acquired with a primary beam energy of 3 eV at a resolution of 60–65 cm^{-1} . Sample preparation and cleaning procedures are described elsewhere.^{26,27} The heating rate during temperature programmed reaction was nonlinear but highly reproducible; between 100 and 700 K, the rate was $\sim 7\text{ K/s}$.

The oxygen overlayer coverages were determined from the O(KLL):Mo(LMM) ratios with use of an oxygen overlayer with a known

coverage of 0.35 ML as a standard.²⁸ The 0.3 ML overlayer was prepared by exposing the crystal to O₂ at a chamber pressure rise of 5×10^{-10} Torr for 30 s at 100 K with the crystal approximately 8 mm from the directed dosing tube, and subsequently heating to 300 K at rate of $\sim 7\text{ K/s}$. The 0.5 ML oxygen overlayer was prepared in an identical manner except that the pressure rise was 1×10^{-9} Torr. In both cases, a (1 × 1) LEED pattern was observed. The highest coverage overlayer (0.75 ML) was prepared by dosing oxygen at 1×10^{-9} Torr and 100 K for 60 s with the crystal approximately 3 mm from the directed doser, followed by heating to 760 K. The complex LEED pattern observed for this overlayer is described elsewhere.²⁹ Electron energy loss data show that quasi-3-fold sites are populated between 0.3 and 0.75 ML and subsurface oxygen is also present for the 0.75 ML oxygen overlayer.

The sulfur overlayers were prepared by exposing the surface to a saturation dose of H₂S and annealing for 60 s at various temperatures. For the 0.25 and 0.4 ML coverages, H₂S was dosed at 100 K, and the crystal was annealed to 1690 and 760 K, respectively. The 0.5 ML overlayer was prepared by exposure at 1390 K followed by annealing at 1390 K. A sharp p(4 × 1) LEED pattern was observed for the 0.5 ML overlayer, and the S(KLL):Mo(LMM) Auger ratio for this overlayer was used to calibrate the other sulfur coverages.³⁰ The LEED patterns were c(2 × 2) for the 0.4 ML overlayer and a mixture of c(2 × 2) and p(2 × 2) for the 0.25 ML overlayer.

The ethanol (Pharmco, 99%) and CD₃CD₂OD (98% d, Cambridge Isotope Laboratories) were stored in glass bottles over molecular sieves. The samples were subjected to several freeze–pump–thaw cycles before use, and their purities were confirmed by mass spectrometry.

Results

Previous studies of ethanol reaction on Mo(110) have shown that ethoxide is formed via O–H bond scission after heating to 300 K.^{31,32} The primary gaseous carbon-containing product formed during temperature programmed reaction of ethanol is ethylene, peaking at 420 K with a shoulder at $\sim 500\text{ K}$ (Figure 1). In addition, H₂ is evolved in two peaks at 420 and 510 K, and a minor amount of ethane formed at 400 K accounts for approximately 4% of hydrocarbon production.³² Residual carbon and oxygen are also detected by Auger electron spectroscopy after temperature programmed reaction to 760 K. On the basis of the O(KLL) signal, the amount of ethanol that irreversibly reacts is estimated as 0.37 ML, given that no oxygen-containing products leave the surface. Furthermore, the C(KLL):O(KLL) Auger ratio indicates that the selectivity for hydrocarbon production is $\sim 40\%$.

The presence of oxygen in the quasi-3-fold coordination sites increases the selectivity and temperature of ethylene formation. Ethylene, H₂O, and H₂ are the major gaseous products formed in the temperature programmed reaction of ethanol on the oxygen overlayers (Figure 1). The lack of 30 amu signal shows that ethane is not produced. In addition to condensed ethanol sublimation at 160 K, a molecular ethanol desorption state around 230 K becomes more pronounced for the higher oxygen coverages (data not shown). A small amount of acetaldehyde, which was barely detectable, was produced at 550 K on the 0.75 ML overlayer; acetaldehyde was identified by comparison of the observed 29:44 amu ratio to that of an authentic sample of acetaldehyde, and to the 30:48 amu ratio from acetaldehyde-*d*₄ produced in the ethanol-*d*₆ reaction. No acetaldehyde was produced for other oxygen coverages. A broad mass scan from

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(28) Methanol decomposition on Mo(110) leaves 0.35 ML of oxygen on the surface, according to X-ray photoelectron studies.²⁵

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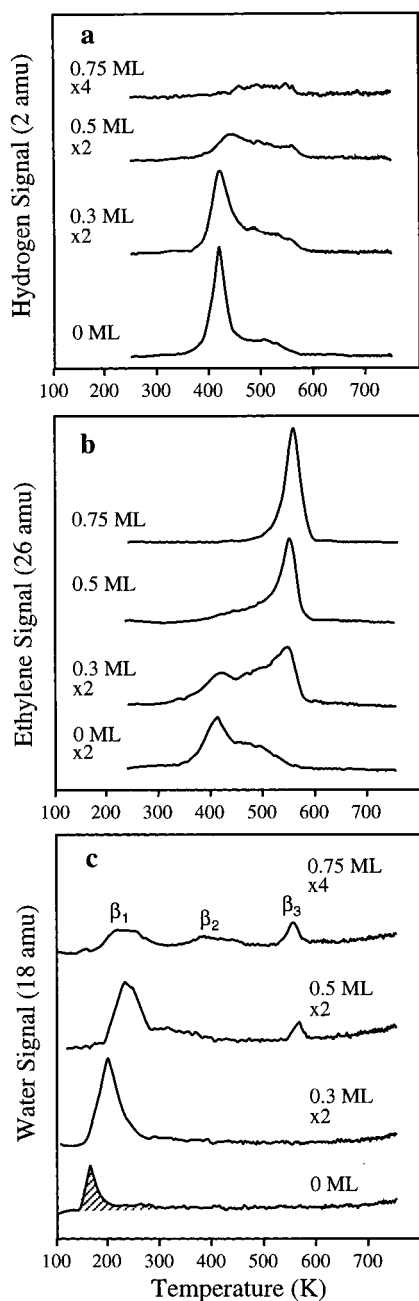


Figure 1. Temperature-programmed reaction of ethanol on various oxygen overlayers: (a) H_2 (2 amu); (b) ethylene (26 amu); (c) H_2O (18 amu). The shaded region in (c) represents desorption from contaminant H_2O in the ethanol sample.

0 to 80 amu illustrated that no other gaseous products were formed. Product identification was based on a comparison of the fragmentation patterns with those of authentic samples.³³ Notably, there is no evidence for a kinetic isotope effect in the ethylene production upon deuteration; the ethylene evolution temperature is the same for reaction of ethanol- d_0 and - d_6 on the 0.75 ML overlayer. Therefore, C–H bond scission is *not* the rate-limiting step in ethylene production.

The peak shapes for ethylene and H_2 evolution change significantly as a function of oxygen coverage (Figure 1b,c). Ethylene is produced at 420 and 545 K on a surface containing

(33) The 26:27 and 27:28 amu ratios for ethylene, and the corresponding ions for ethylene- d_4 produced from ethanol- d_6 reaction, were used to identify ethylene. Similarly, the 17:18 amu ratio for H_2O and 18:20 amu ratio for D_2O from ethanol- d_0 and - d_6 reaction, respectively, confirmed the product assignment as water.

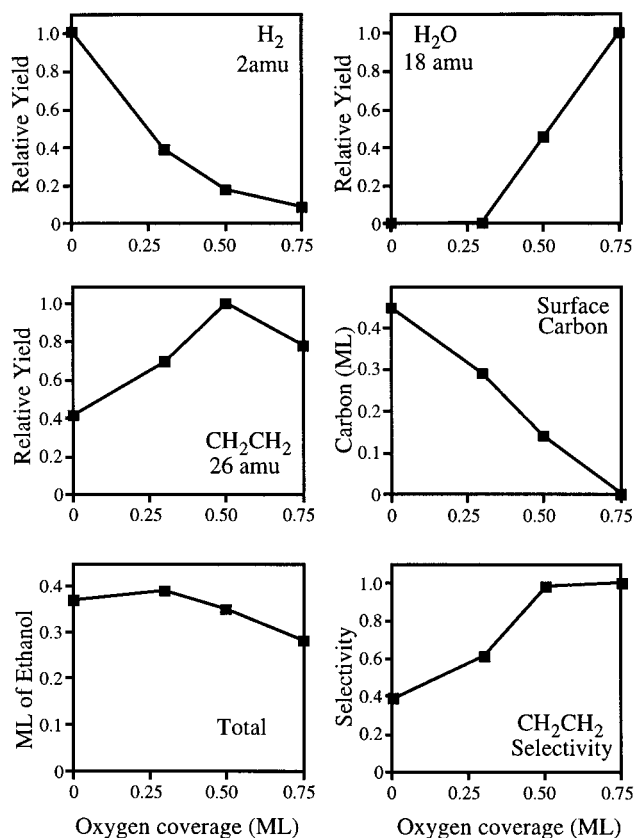


Figure 2. Product distributions for ethanol reaction as a function of oxygen coverage. The H_2O yield is only for evolution at 550 K. Yields for H_2 , H_2O , and ethylene are normalized by dividing by the maximum value for each plot.

0.3 ML of oxygen, similar to what is observed on Mo(110). However, the intensity of the ethylene peak at 545 K is greater relative to the 420 K peak on the oxygen-covered surface. As the oxygen coverage is increased to 0.5 ML, the high-temperature ethylene peak at 550 K becomes the dominant feature, and the 420 K peak is only observed as a shoulder around 400 K. On the 0.75 ML overlayer, ethylene is produced in a narrow, asymmetric peak at 560 K while the lower temperature state is absent. The total H_2 signal decreases with oxygen coverage, with the 520 K state losing intensity less rapidly than the 420 K state. The decrease in H_2 yield coincides with a monotonic increase in H_2O yield, indicating that the hydrogen liberated by ethylene formation is mainly evolved as H_2O for initial oxygen coverages in the range of 0.5–0.75 ML (Figure 2). Almost no H_2 is produced from ethanol reaction on the 0.75 ML oxygen overlayer.

Water production at ~ 200 K (β_1) occurs on all of the oxygen overlayers, which shows that the O–H bond of ethanol is broken at low temperature (Figure 1c). A distinct H_2O peak at 550 K appears for coverages ≥ 0.5 ML, and H_2O is also produced in a broad peak (β_2) between 300 and 500 K during reaction on the 0.75 ML overlayer. Ethanol reaction on an ^{18}O -labeled overlayer (0.75 ML) produced only H_2^{18}O in the β_1 and β_2 states, demonstrating that they arise from reaction of hydrogen with preadsorbed oxygen. The mixture of H_2^{16}O and H_2^{18}O evolved at 550 K indicates that the production of β_3 H_2O water involves both oxygen adsorbed prior to reaction and oxygen deposited as ethylene is formed.

Oxygen also increases the selectivity for ethylene formation over nonselective decomposition without severely inhibiting ethanol reaction for coverages below 0.50 ML (Figure 2). The

monotonic decrease in both the H₂ and surface carbon yields with increasing oxygen coverage reflects a decrease in the nonselective decomposition pathway. At the same time, the ethylene yield initially increases for oxygen coverages up to 0.5 ML. The net result is a nearly constant amount of irreversible ethanol reaction and an increase in the selectivity for ethylene production (Figure 2).³⁴ The selectivity for ethylene production increases from 40% on clean Mo(110) to nearly 100% for oxygen coverages above 0.5 ML. A reduction in the total amount of irreversible ethanol reaction occurs for coverages ≥ 0.5 ML, but approximately 0.3 ML of ethanol reacts even for an oxygen coverage of 0.75 ML.

Population of Mo=O sites and dissolution of oxygen into the bulk leads to a substantial reduction in the amount of ethanol reaction on Mo(110). The doubly bound, terminal oxygen site is populated by using higher oxygen exposures and temperatures. For example, electron energy loss studies show a ~ 1.7 ML overlayer prepared by oxygen exposure at 1200 K^{29,35} is comprised of oxygen at terminal and quasi-3-fold as well as subsurface sites.^{18,19} The total amount of ethanol that reacts on this surface is $\sim 4\%$ compared to clean Mo(110), and ethylene is formed in a very broad feature extending between 350 and 650 K (data not shown). Depopulation of the Mo=O sites is achieved by heating to 1400 K, which drives oxygen into the bulk and creates vacancies in high coordination sites based on our recent studies of methanol on oxidized Mo(110).⁶² The amount of irreversible ethanol reaction on the resulting overlayer is increased relative to the surface containing Mo=O, to $\sim 28\%$ that of Mo(110). Furthermore, the narrow, asymmetric peak shape for ethylene evolution at 550 K is the same as that observed for the 0.75 ML overlayer.

Ethoxide and OH are identified on the oxygen overlayers ($\theta_{\text{O}} = 0.3\text{--}0.75$ ML) by using electron energy loss spectroscopy (Figure 3). The electron energy loss spectra for ethanol heated to 300 K on the oxygen overlayers are very similar to the spectra of ethoxide on Mo(110),³¹ Rh(111),³⁶ Pd(111),³⁷ and oxidized Cu(111).³⁸ Note that the O–H stretch for intact ethanol, which should appear at ~ 3250 cm⁻¹,^{31,36} is not observed. Mode assignments for ethoxide on oxygen-covered Mo(110) are based on a normal-mode analysis of ethoxide on Mo(110)³¹ and are consistent with the assignments for ethoxide on Rh(111), Pd(111), and oxygen-covered Cu(111) (Table 1). Furthermore, the normal-mode analysis shows that $\nu(\text{C-O})$ and $\nu(\text{C-C})$ are strongly coupled with each other and with $\rho(\text{CH}_3)$ due to their similar force constants. The $\nu(\text{C-O})$ and $\nu(\text{C-C})$ modes are more accurately described as $\nu_{\text{a}}(\text{C-C-O})$ and $\nu_{\text{s}}(\text{C-C-O})$.³⁹

Surface OH is also present after heating ethanol to 300 K, indicating that oxygen in high coordination sites reacts readily with the alcoholic proton of ethanol. Adsorbed hydroxyl is signified by the loss at 3557 cm⁻¹, for oxygen coverages ≥ 0.5 ML (Figure 3b). The 3557 cm⁻¹ peak is assigned to $\nu(\text{O-H})$

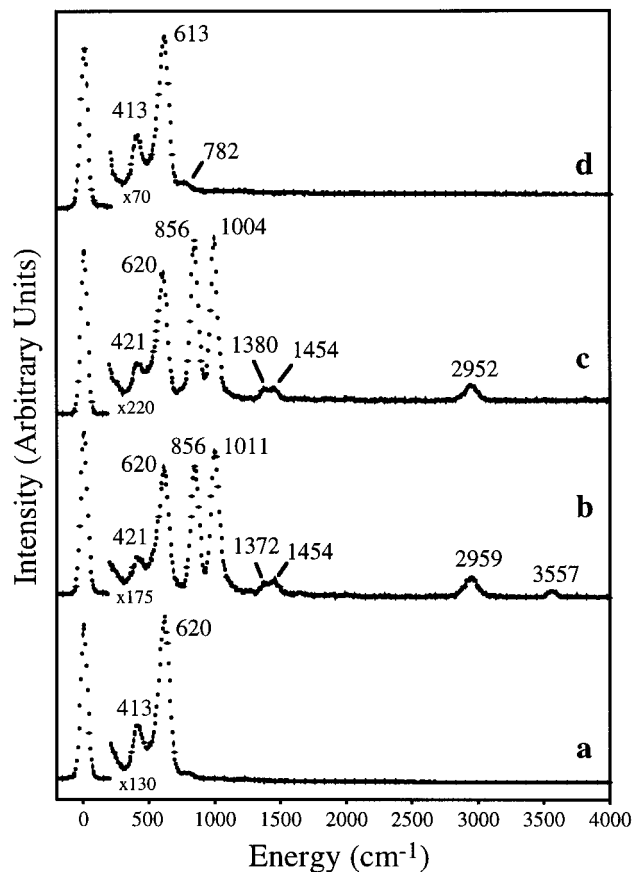


Figure 3. Electron energy loss spectra for (a) 0.75 ML oxygen overlayer and ethanol on the 0.75 ML oxygen overlayer heated to (b) 300, (c) 500, and (d) 760 K.

Table 1. Assignments for Ethanol on Various Oxygen and Sulfur Overlayers on Mo(110), Flashed to 300 K

Mo(110)	O–Mo(110)			S–Mo(110) 0.4 ML	assignment
	0.3 ML	0.5 ML	0.75 ML		
		3557	3557		hydroxyl $\nu(\text{O-H})$
2930	2937	2944	2959	2944	$\nu(\text{C-H})$
1446	1446	1454	1454	1454	$\delta_{\text{a}}(\text{CH}_3)$
1365	1372	1372	1372	1365	$\delta_{\text{s}}(\text{CH}_3)$, $\omega(\text{CH}_2)$
1041	1033	1011	1011	1011	$\nu_{\text{a}}(\text{C-C-O})$, $\rho(\text{CH}_3)$
878	878	863	856	856	$\nu_{\text{s}}(\text{C-C-O})$
539	553	613	620	509	$\nu(\text{Mo-O})/\nu(\text{Mo-S})$, $\nu(\text{Mo-OR})$
			421	398	$\delta(\text{Mo-O})$, $\delta(\text{CCO})$

of surface hydroxyl, based on studies of OH on other surfaces,⁴⁰ and based on the good agreement with the value of 3550 cm⁻¹ measured after heating H₂O to 300 K on the 0.75 ML oxygen overlayer.⁴¹ The absence of intensity in the 1600 cm⁻¹ region from $\delta(\text{H-O-H})$ indicates that molecular H₂O is not present on the surface.

After heating ethanol on the 0.75 ML oxygen overlayer to 500 K, the modes of ethoxide remain, but $\nu(\text{O-H})$ disappears (Figure 3c). This is consistent with the observation of H₂O evolution between 300 and 500 K, and further indicates that ethoxide remains intact up to the onset of ethylene production. After heating to 760 K, the modes at 613 and 413 cm⁻¹ are attributed to $\nu(\text{Mo-O})$ and $\delta(\text{Mo-O})$, and the feature at 782 cm⁻¹ to subsurface oxygen.^{29,18} These data clearly show that

(34) The correspondence between the integrated ethylene signal in the temperature programmed reaction and ethylene production in ML was determined from the ethylene yield, total amount of reaction in ML, and selectivity for hydrocarbon formation from ethanol reaction on Mo(110). Note that ethane production on Mo(110) was negligible ($\sim 4\%$).

(35) This high coverage oxygen overlayer is prepared by exposing the crystal to 1×10^{-9} Torr of O₂ at 1200 K for 5 min; the coverage estimated from the O(1s) signal is 1.7 ML, which is a lower limit because subsurface oxygen forms under these preparation conditions.¹⁸ The coverage was previously reported incorrectly as 0.33 ML.⁴¹

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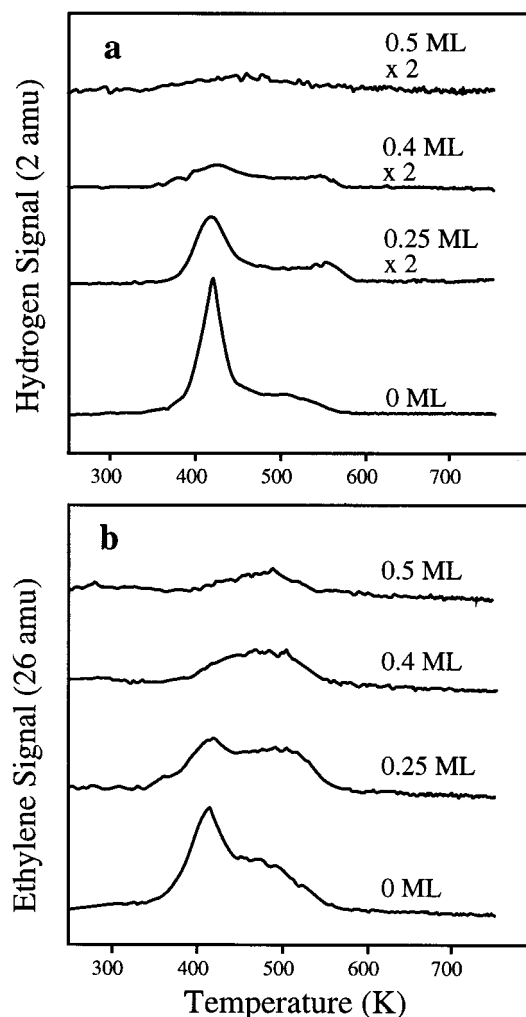


Figure 4. Temperature-programmed reaction of ethanol on various sulfur overlayers: (a) H_2 (2 amu); (b) ethylene (26 amu).

the ethoxide reaction does not leave oxygen at the terminal sites. Terminal oxygen would be signified by a $\nu(\text{Mo}=\text{O})$ peak near 1000 cm^{-1} .

Reaction on Sulfur-Covered Mo(110). The effect of sulfur on ethanol decomposition was studied to probe the relative importance of electronic and site blocking effects. Again, ethylene and H_2 are the only gaseous products observed in the temperature programmed reaction of ethanol on the sulfur overlayers (0.25–0.5 ML). A low-temperature molecular ethanol desorption state grows in around 230–250 K with increasing sulfur coverage. A broad mass scan between 0 and 80 amu showed that no other products were evolved. Specifically, no ethane, formaldehyde (29,30 amu), or sulfur-containing products (32 amu) were detected. Carbon and oxygen are detected by Auger spectroscopy after heating to 760 K for sulfur coverages below 0.4 ML.

The peak temperatures for H_2 and ethylene evolution do not change with sulfur coverage (Figure 4). On the overlayer containing 0.25 ML of sulfur, H_2 is evolved in two states at 410 and ~ 530 K. As the sulfur coverage is increased, the total H_2 yield decreases such that H_2 is formed in a broad feature between 350 and 550 K on the 0.5 ML overlayer. Although ethylene evolution occurs at around 410 and 500 K on all of the sulfur overlayers, the intensity of the 500 K peak decreases less rapidly than the 410 K peak with increasing sulfur coverage.

The product yields for ethanol reaction as a function of sulfur coverage demonstrate that the main effect of sulfur is to decrease

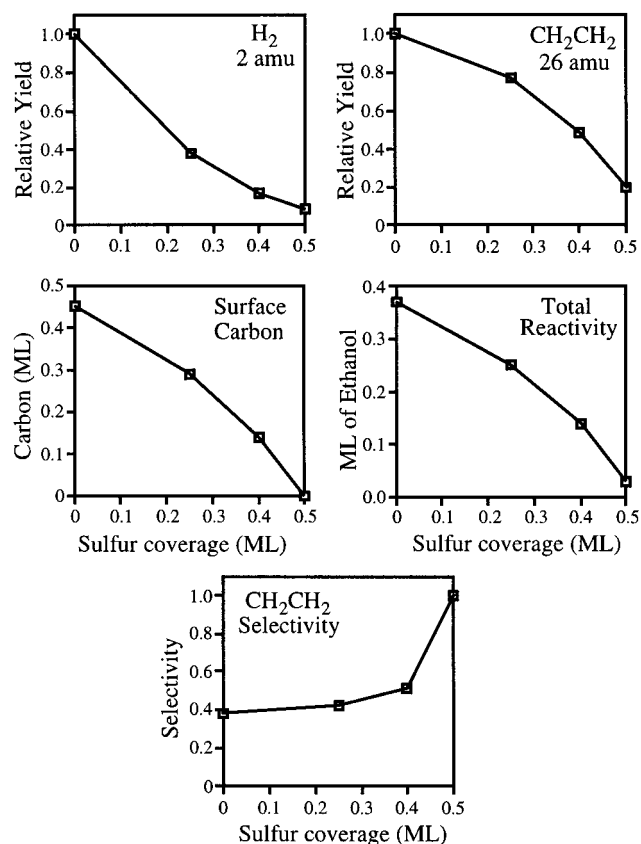


Figure 5. Product distributions for ethanol reaction as a function of sulfur coverage. Yields for H_2 and ethylene are normalized by dividing by the maximum value for each plot.

the total amount of irreversible ethanol reaction (Figure 5). The yields of all products— H_2 , ethylene, and surface carbon—decrease uniformly with increasing sulfur coverage. As the sulfur coverage is increased to 0.25 ML, the selectivity for ethylene formation is essentially unchanged. The amount of ethanol that decomposes when 0.5 ML of sulfur is present is negligible. Ethylene is the sole product detected from the small amount of ethanol reaction—there is no detectable residual carbon.

The vibrational spectrum of ethanol on the 0.4 ML sulfur overlayer after heating to 300 K indicates that ethoxide is formed (Table 1). After heating to 760 K, the losses at 384 and 590 cm^{-1} are assigned to metal-O and metal-S modes, based on comparison to the oxygen- and sulfur-covered surfaces, respectively. The 590 cm^{-1} frequency is characteristic of oxygen in the quasi-3-fold sites.

Discussion

Oxygen and sulfur have markedly different effects on the reactions of ethanol on Mo(110) as a result of their different adsorption characteristics. The monotonic reduction in the amount of ethanol decomposition, approaching zero for a sulfur coverage of 0.5 ML, can be entirely explained by site blocking. Studies of alcohol reaction on sulfur-covered $\text{Fe}(100)^{42}$ and $\text{Ni}(100)^{43}$ have similarly demonstrated that methanol reaction is decreased as a result of site blocking by sulfur. Sulfur is known to occupy high coordination sites on Mo(110)²⁰ and to

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have a maximum coverage of 0.5 ML.⁴⁴ Indeed, a scale model of sulfur bound to Mo(110)⁴⁵ indicates that adjacent high coordination sites are blocked when sulfur is bound to the low-symmetry, high coordination site derived from tensor LEED analysis.²⁰ Sulfur would similarly block the adsorption of ethoxide to high coordination sites neighboring those occupied by sulfur. Theoretical studies of methoxide on Mo(110),²¹ Cu(100),²³ and Ni(111)²² show that alkoxides prefer to adsorb at high coordination sites. Hence, the presence of sulfur is expected to lead to the observed steady decrease in the amount of ethanol decomposition such that no decomposition would occur on an overlayer containing 0.5 ML of sulfur, because all high coordination sites would be obscured by sulfur. Importantly, sulfur does not migrate below the surface plane^{46,47} nor is there any evidence for SH_a or H₂S formation.

In contrast, oxygen bound to high coordination sites does *not* significantly reduce the amount of irreversible ethanol reaction until high coverages. Oxygen increases the selectivity for ethylene elimination from ethanol, while the total amount of irreversible reaction remains significant even up to oxygen coverages of 0.75 ML. There is only minimal reduction in the amount of ethanol reaction at oxygen coverages of 0.50 ML (Figure 2). The sustained activity for ethanol decomposition is attributed to the fact that oxygen is considerably smaller in diameter than sulfur and to the fact oxygen occupies both long-bridge and low-symmetry sites. Because of the smaller diameter of oxygen, additional oxygen is not sterically blocked from high coordination sites adjacent to sites in the [100] direction—either high coordination or long-bridge—occupied by oxygen. The Mo–Mo spacing is 3.15 Å in the [100] direction and the van der Waals radius of oxygen is 1.4 Å.⁴⁸ By the same token, these high coordination sites will still be available for ethoxide binding even when the adjacent high coordination site is occupied by oxygen. These conclusions are consistent with our experimental observation that the amount of irreversible ethanol reaction remains essentially constant up to a coverage of 0.5 ML of oxygen. The similarity in the diameter of oxygen (2.8 Å) and the closest-packed distance on Mo(110) (2.72 Å) suggest that adjacent sites along the closest-packed direction will be more difficult to fill; thus, a coverage of 1.0 ML cannot be readily achieved. We are currently in the process of more closely examining the oxygen overlayer structure above 0.5 ML.

The other possible factor that may lead to sustained ethanol decomposition is the reaction of the chemisorbed oxygen with the alcoholic proton of ethanol to form OH_a. The formation of the O–H would also reduce the charge and hence the size of the oxygen. Furthermore, the most favorable coordination site for OH may be different than oxygen. Both of these factors potentially would reduce the degree of site blocking by the oxygen.

It is also possible that ethoxide displaces some oxygen to the subsurface region or to Mo=O sites. This scenario is unlikely, however, since temperatures in excess of 600 K are required before any subsurface oxygen is detected in electron energy loss experiments. The required thermal activation

(44) Higher effective coverages of sulfur were achieved via S₂ adsorption on Co-, Ni-, and Fe-covered Mo(110).^{61,47} However, the higher sulfur concentrations were associated with dissolution of sulfur into the bulk to make a MoS₂ film. The dissolution was promoted by the metal thin films.

(45) The van der Waals radius of sulfur is 1.85 Å,⁴⁸ rendering a closest-packed distance of 3.70 Å. The lattice constant of Mo(110) is known to be 2.72 Å.

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indicates that migration of oxygen into the bulk or to other sites is highly unlikely at the temperature where O–H bond scission occurs, ~200 K. After heating to 760 K, there is no detectable $\nu(\text{Mo}=\text{O})$ mode whereas subsurface oxygen, signified by a peak at 782 cm⁻¹, is clearly present. Hence, displacement of oxygen to terminal sites does *not* occur. We attribute the peak at 782 cm⁻¹ to oxygen that dissolves into the bulk at temperatures above 600 K, after C–O bond breaking.

Our studies of ethanol reaction on the high-coverage oxygen overlayers (~1.7 ML) also provide evidence that the Mo=O species do not promote ethanol reaction. Oyama et al. have proposed that oxygen at terminal sites is responsible for the partial oxidation of ethanol to acetaldehyde,^{10–13} and investigations of methanol oxidation to formaldehyde over Mo oxides have also suggested that oxidation activity occurs at terminal oxygen sites.^{3,6} However, ethanol reaction was *not* promoted in the presence of the Mo=O species; in fact, the amount of irreversible ethanol reaction was significantly decreased, and no acetaldehyde was produced. Furthermore, depopulation of the terminal sites by heating to 1400 K did not restore reactivity to the value observed on the 0.75 ML oxygen overlayer, indicating that terminal oxygen is not responsible for blocking reaction on the highly oxidized surface. Although heating to 1400 K did increase the amount of ethanol reaction from 4% to 28% of that on Mo(110), recent studies of the effect of annealing time on methanol reaction provide strong evidence that vacancies in high coordination sites are also created upon heating to 1400 K.⁶² While our studies rule out the possibility that Mo=O moieties promote ethanol reaction, we cannot rule out changes in selectivity associated with them.

It is important to note that oxidized Mo(110) exhibits reactivity different than bulk MoO₃—probably because of the lower degree of Mo oxidation on Mo(110). Acetaldehyde is the major product of ethanol reaction on MoO₃, whereas ethylene is the primary product on oxidized Mo(110). We propose that C–O bond scission primarily occurs at open, high coordination sites on Mo(110). In our model system, the bulk of Mo(110) is a sink for oxygen, and there are vacancies in high coordination sites even at the highest oxygen coverages investigated, 1.7 ML. In contrast, bulk MoO₃ will have a limited ability to take up additional oxygen due to its high oxidation state. Furthermore, vacancies in the bulk oxide are most likely to occur at Mo=O sites because of their lower coordination number. Therefore, C–O bond retention is favored on the bulk oxide, where oxygen vacancies are required to deposit oxygen.

The different oxidation states of the model Mo(110) and bulk MoO₃ may also change the facility for C–O and C–H bond breaking via electronic effects. The C–O bonds of alkoxides, e.g., CH₃O, on Mo(110) are strongly perturbed, leading to a substantial reduction in the C–O bond strength.⁶³ The Mo centers in MoO₃ are electron deficient and, therefore, will not be as effective as electron donors as the lower-valent Mo centers. We are planning to address this point by performing electronic structure calculations.

The enhanced selectivity for ethylene production from ethanol reaction on oxidized Mo(110) may arise from reduced activity for either C–H or C–C bond scission. In reactions of methanol on oxygen-covered Mo(110), methyl radical production is favored over decomposition to carbon and oxygen, suggesting that the presence of oxygen inhibits C–H bond breaking and allows for homolytic C–O bond breaking.⁴⁹ By analogy, we propose that ethylene is formed via homolytic C–O bond

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breaking in ethoxide, yielding a transient ethyl radical and surface-bound oxygen. Ethylene would subsequently be formed via hydride elimination from the radical; ethylene production from ethyl has been observed on oxygen-covered Rh(111),⁵⁰ Ni(100),⁵¹ Pt(111),⁵² and Cu(111).⁵³ The hydrogen eliminated from the ethyl radical would then react with oxygen on the surface to produce H₂O, thus opening sites for further C–H bond breaking by the metal. This mechanism is consistent with all of our data and specifically rationalizes the absence of a kinetic isotope effect in ethylene formation upon deuteration of ethanol. Furthermore, it qualitatively accounts for the apparent acceleration in the rate of ethylene production, which results in the sharp, asymmetric shape for the ethylene peak. Such line shapes have been attributed to autocatalytic processes in several other surface reactions.^{54,55}

The inhibition of nonselective C–H bond breaking on oxidized Mo(110), compared to less significant changes on sulfur-covered Mo(110), suggests that modification of the surface electronic structure plays an important role. Both oxygen and sulfur are expected to create a deficiency of electron density at the surface that could prevent electron donation from the metal orbitals to the antibonding orbitals of the adsorbed molecule. However, the sulfur is expected to result in a smaller perturbation of the local electronic structure because of its lower electronegativity relative to oxygen. Furthermore, high coordination sites adjacent to those occupied by sulfur are blocked with respect to ethoxide coordination whereas sites adjacent to those occupied by oxygen are available to ethoxide. Accordingly, the possibility of more proximal bonding of ethoxide to oxygen is expected to lead to a greater electronic effect relative to sulfur. In fact, the selectivity for ethylene production in ethanol reaction increases more rapidly as a function of oxygen coverage than it does over the same coverage regime for sulfur. On the oxygen-covered surface, selectivity is increased from 38% on the clean surface to 61% on the 0.3 ML overlayer, whereas for sulfur the selectivity is essentially unchanged over the same coverage range. On Fe(100)⁴² and Mo(211),⁵⁶ oxygen has also been proposed to create a surface electron deficiency that inhibits interaction between alkyl hydrogen and the metal, thereby passivating the surface for C–H bond breaking in methoxide.

We propose that the two distinct ethylene states from ethanol reaction on oxygen-covered Mo(110) ($\theta_{\text{O}} \geq 0.5$ ML) could be

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associated with sites that are not adjacent to those occupied by oxygen (410 K) and those proximal to oxygen in high coordination sites (550 K). In contrast, there is a single ethylene peak on the sulfur-covered surfaces, which decreases in intensity but does not shift as a function of sulfur coverage. These data are again consistent with our proposal that ethoxide can occupy high coordination sites adjacent to those occupied by oxygen, but not those adjacent to sites occupied by sulfur.

Notably, oxygen on Mo(110) neither inhibits nor promotes reaction, but instead enhances selectivity. On many transition metal surfaces, adsorbed oxygen inhibits alcohol reactions in a manner similar to sulfur. For example, the presence of surface oxygen on Fe(100),^{57,58} Fe(110),⁵⁹ and Co thin films deposited on Mo(110)⁶⁰ decreases the total amount of alcohol reaction and favors reversible, molecular desorption over O–H bond scission. Interestingly, the lattice constants are considerably smaller for these materials than for Mo. The lattice constants for Fe and Co are 1.24 and 1.25 Å, respectively, compared to 1.36 Å for Mo. These observations further support our geometric argument regarding the lack of site blocking by oxygen on Mo(110).

Conclusions

The addition of oxygen or sulfur as a surface modifier causes a dramatic increase in the selectivity for ethylene production versus nonselective decomposition in the deoxygenation of ethanol on Mo(110). Reactivity is not significantly reduced even for an oxygen coverage of 0.50 ML, but sulfur decreases surface reactivity to <10% that on Mo(110) at 0.5 ML. The high reactivity sustained on the oxygen overlayers is explained on the basis of its diameter relative to the Mo–Mo lattice spacing and its ability to form adsorbed OH from reaction with hydrogen. The inhibition of ethanol decomposition on the sulfur overlayers is attributed to a site blocking effect. Increased selectivity for ethylene production on both the oxygen and sulfur overlayers is proposed to arise from electronic surface modification.

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