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Relationship of Bond Strengths to Selectivity in Heterogeneous Surface Reactions: Mercaptoethanol and Ethanedithiol on Ni(110)

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The reaction selectivities and bonding configurations in mercaptoethanol ($HSCH_2CH_2OH$) and ethanedithiol ($HSCH_2CH_2SH$) on Ni(110) were determined and found to be correlated to the relative strengths of the C−S and C−O bonds. Mechanistic details of the mercaptoethanol reaction have been elucidated. Mercaptoethanol reacts with Ni(110) to form ethanol, acetaldehyde, methane, CO, and hydrogen. Mercaptoethanol reactivity is dominated by thiolate formation as suggested by the S 2p core level binding energy. Near 200−250 K, the C−S bond cleaves with the evolution of ethanol and formation of surface ethoxide which is easily discernible from vibrational spectroscopy. The ethoxide dehydrogenates to form acetaldehyde, which either desorbs or reacts to form methane and CO. In dramatic contrast, the structurally similar ethanedithiol apparently adsorbs in a bidentate fashion, resulting in a dithiolate which selectively splits out ethylene and produces surface sulfur. The difference in the reactivity of ethanedithiol and mercaptoethanol is understood in terms of the inactivity of the Ni(110) surface toward C−O bond scission, which is primarily a reflection of the strength of C−O bonds compared with C−S bonds.

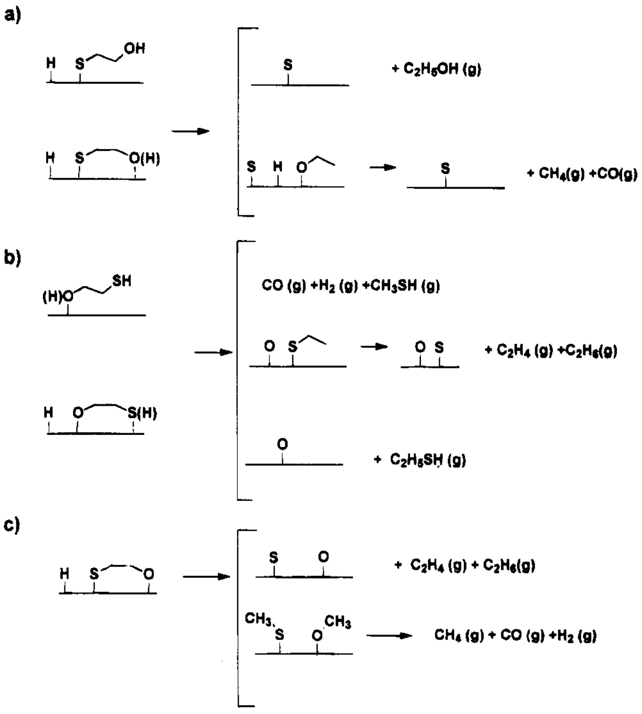
Introduction

Studies of reactions on single crystal surfaces afford the opportunity to identify reaction intermediates spectroscopically and to examine reaction mechanisms at a molecular level. In most studies, the organic adsorbates are simple, monofunctional molecules so that detailed information about reactions of that specific functionality with a given surface is obtained. Rarely are multiple reactive functionalities present in adsorbates, despite the significance of reaction selectivity in catalytic systems. The primary goal of this study is to examine the selectivity of reaction products from polyfunctional molecules on a single crystal metal surface, specifically Ni(110).

Under industrial hydrodesulfurization conditions, catalysts are exposed to a variety of chemical functionalities, including sulfhydryl groups, thiophenic sulfur, hydroxyl groups, and aromatic and aliphatic hydrocarbons. Previous studies in our laboratory have examined reactions of alkanethiols (methanethiol[1,2] and ethanethiol[3]), aryl thiols (benzenethiol and methylbenzenethiol[4,5]), and H_2S[6,7] on clean, and hydrogen and oxygen predosed Ni surfaces. In addition, reactions of methanol and ethanol have been studied on nickel surfaces.[8−11] This paper utilizes that knowledge of thiol and alcohol chemistry on Ni(110) and extends it by examining the reaction of mercaptoethanol ($HSCH_2CH_2OH$), where both sulfhydryl and hydroxyl groups are present. Adsorption and reactions of several structurally related molecules, ethanedithiol ($HSCH_2CH_2SH$), ethanethiol, and ethanol, were studied to aid in the identification of intermediates and the elucidation of mechanistic detail. The overall goal of this work was to identify and understand the reaction selectivity when both sulfhydryl and hydroxyl groups are present within one molecule.

The key issues to be examined are the bonding configuration of mercaptoethanol and the reaction selectivity. Thiols are known to undergo dissociative adsorption, with cleavage of the sulfhydryl bond on Ni surfaces at 100 K producing surface thiolate species.[1,2,4,5,12−15] Alcohols can adsorb molecularly or as the analogous alkoxides. In principle then, mercaptoethanol is likely to bond through the sulfur atom as a thiolate, through the oxygen atom as an alkoxide or alcohol, or potentially in a bidentate fashion. Energetically, the latter is probably favored since both thiolates and alkoxides form strong bonds to metal surfaces[16−18] and since the surface metallocycle formed would be at least a five-membered ring and, therefore, not sterically strained. However, at high coverages, surface crowding may force a monodentate adsorption through either the sulfur or the oxygen. Since the adsorption energies of the thiolates and alkoxides are very similar, there might be a mixture of bonding configurations. The adsorption geometry is expected to strongly influence the reaction selectivity as summarized in Scheme 1. On Ni(110), thiols react near 200−250 K to form hydrocarbons.

SCHEME 1



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If mercaptoethanol forms β-hydroxyethyl thiolate (Scheme 1a), the analogous reaction would produce ethanol near 250 K. The ethanol could either desorb or remain on the surface, bonded through the oxygen as ethoxide. Although reactions of ethanol on Ni(110) have not been previously reported, on Ni(111), C−H and C−C bond scissions occur preferentially to C−O bond scission,[10] so methane and CO are the likely products of ethoxide decomposition. If β-mercaptoethoxide (Scheme 1b) were present, methanethiol, CO, and hydrogen might be the expected products. However, if the C−O bond were activated, ethanethiol or surface ethyl thiolate might be observed. Alternatively, if a bidentate species forms (1c), the C−O bond could be activated so that simultaneous or sequential C−O and C−S bond scission may produce ethylene or ethane (since surface hydrogen would also be present from cleavage of the sulfhydryl and hydroxyl bonds). Cleavage of the C−C bond could result in methane, methanethiol, or methanol formation.

Similarly, ethanedithiol could adsorb in either a bidentate or a monodentate configuration. A bidentate configuration would be expected to produce C_2 hydrocarbons or, if the C−C bond were activated, methane. A monodentate configuration could result in the formation of β-mercaptoethyl thiolate which, upon C−S bond scission, could produce both ethanethiol and ethyl thiolate. Ethyl thiolate would then produce ethane, ethylene, hydrogen, and surface sulfur.[3]

The approach taken in this study is to examine these reactions under ultrahigh-vacuum (UHV) conditions on an initially clean Ni(110) crystal. A variety of techniques were used to examine various aspects of the reaction sequence. The formation of gas phase products was monitored by temperature-programmed reactions (TPR). Surface intermediates were identified by X-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss spectroscopy (HREELS). Auger electron spectroscopy (AES) and XPS were used to determine surface coverages of strongly adsorbed atomic species. Finally, further confirmation of reaction pathways was made by adsorbing related compounds and comparing TPR desorption profiles.

Experimental Section

These experiments were performed in a stainless steel UHV chamber (base pressure 7×10^{-11} Torr) equipped with a double pass cylindrical mirror analyzer for AES and XPS measurements, a quadrupole mass spectrometer for TPR measurements, a high resolution electron energy loss spectrometer (HREELS), and a four-grid low-energy electron diffraction (LEED) system. A nickel single crystal rod was cut to within 0.75° of the 110 face producing a 8 mm diameter disk, roughly 1 mm thick. This disk was mechanically polished. Prior to introduction to the UHV system, the single crystal disk was heated in 1 atm of H_2 at 940 K to remove any impurity sulfur from the bulk of the Ni crystal. The crystal was mounted on a specimen manipulator and could be cooled to 90 K and heated to 1200 K. The sample temperature was measured with a chromel−constantan (type E) thermocouple spot-welded to the back of the crystal. The sample was cleaned *in situ* by Ne ion sputtering followed by annealing to 1000 K for 60 s. AES and LEED were used to verify cleanliness and crystallographic order, respectively.

The mercaptoethanol (Aldrich) was purified by freeze−pump−thaw cycles each day. Mercaptoethanol vapor was admitted to the UHV chamber through a directed doser. The doser consisted of a glass vial in which the mercaptoethanol was stored, a conductance limiting aperture (8 μm diameter), and a stainless steel dosing tube (0.5 in. diameter). After repeated freeze−pump−thaw cycles, the mercaptoethanol vapor was admitted to the vacuum chamber through the aperture with the sample positioned approximately 1 mm in front of the dosing tube. The dosing rate was regulated by maintaining the liquid in the glass ampule at a constant temperature (283−288 K) and, hence, controlling its vapor pressure. The exposures were terminated by rapidly pumping out the region behind the aperture. Uptake curves as a function of dosing time and mercaptoethanol temperature were obtained and the exposures were found to be quite reproducible and of high purity. The purity of the dosing gas was determined mass spectrometrically, both by comparing mass spectra of the vapor under dosing conditions with literature spectra[19] and by monitoring for ethanol (the most prevalent impurity) by TPR following doses sufficiently large to form films of physisorbed material.

Ethanedithiol was dosed through a similar gas doser, except that because of its higher vapor pressure, the vapor was admitted to a stainless steel reservoir to a desired pressure measured by a capacitance manometer. The ethanedithiol was purified by several freeze−pump−thaw cycles each day, and the purity of the dosing gas was checked as the reservoir was refilled daily.

Desorbed species were monitored mass spectrometrically (up to 6 masses simultaneously) while heating the sample via a feedback controlled linear heating ramp of 5 K/s. The sample was biased to −70 V to eliminate the possibility of electron induced decomposition as is frequently observed in thiol surface chemistry. The XPS data were obtained with Mg or Al anodes under conditions where the instrumental resolution was about 1−1.5 eV as determined by measuring the C 1s spectrum of benzene. The binding energies were referenced to the Ni 2p and 3p core levels (852.8 and 66.5 eV, respectively[20]) from the clean surface. The AES data were measured using a primary electron energy of 3 keV and a modulation voltage of 3 eV_{p-p}.

The sulfur coverages were calibrated by comparing the S(152)/Ni(848) Auger ratios after heating the surfaces to 800 K with those obtained following H_2S adsorption.[6,7] Since no sulfur containing molecules other than physisorbed mercaptoethanol (or ethanedithiol) were observed, the sulfur coverage measured in this way is equivalent to the initial coverage of sulfur in the chemisorbed species.

Results

Desorption Products from Mercaptoethanol. Thermal desorption spectra were obtained as a function of coverage. Because of the multiple reaction pathways possible, a wide variety of products were monitored. The primary reaction products were H_2, CO, methane, and ethanol. Small amounts of acetaldehyde were also observed. There was never any indication of methanethiol, methanol, or ethanethiol in any TPR traces. Detection of ethane and ethylene was somewhat uncertain, because only very weak features for m/e 26 and 30 were observed, which were convoluted with cracking from other products. However, if any C_2 hydrocarbons were produced, they were formed in trace quantities. In some experiments, relatively small amounts of water were observed, but the desorption profiles suggested that the origin of the water was as an impurity in the dosing gas.

H_2 Desorption. The hydrogen temperature programmed desorption profiles are shown in Figure 1a as a function of coverage. At low coverage the desorption profiles are dominated by a single peak near 300 K which initially grows with increasing exposure. This peak is attributed to recombination of surface hydrogen atoms formed from the nonselective decomposition of the mercaptoethanol. The temperature of this peak suggests a desorption limited process indicating that at low coverage decomposition commences below 300 K. At about 0.3 monolayer (ML), a second peak at 265 K is observed, also attributed to desorption limited hydrogen from regions of the surface strongly modified by surface sulfur, an effect

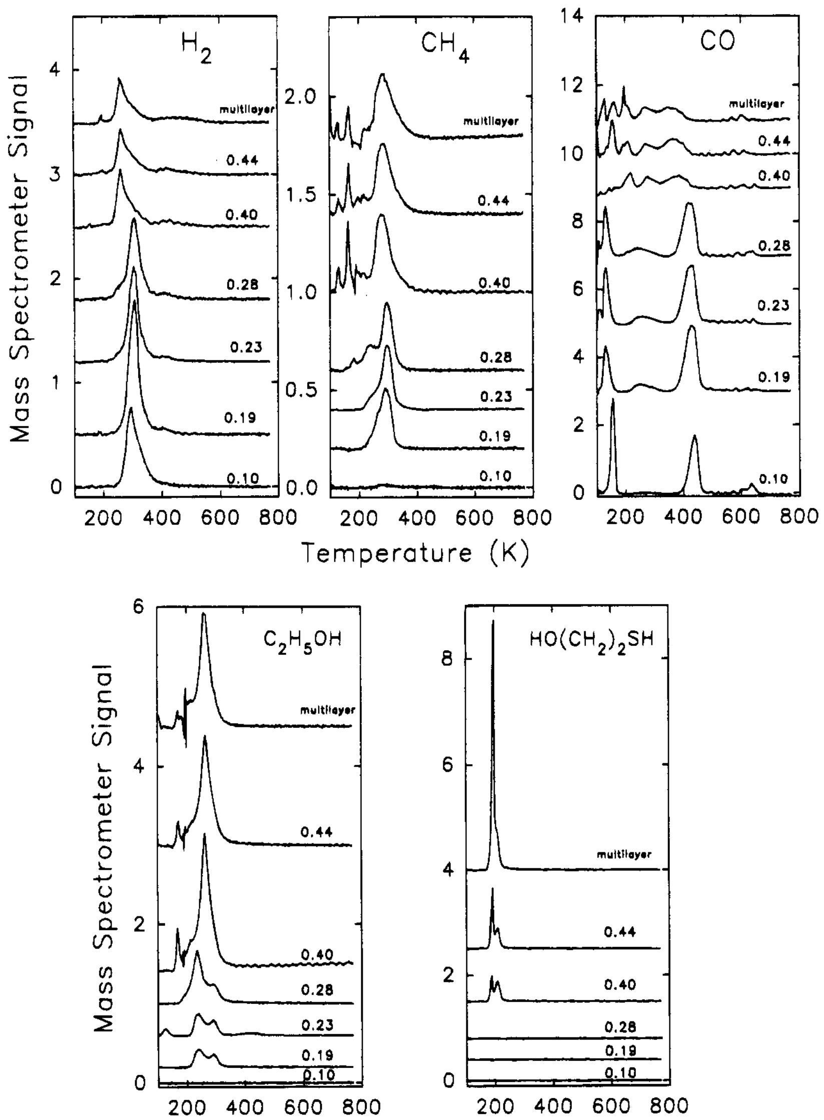

Figure 1. (a) Coverage dependence of the desorption profiles for H_2, CH_4, and CO. The profiles for H_2 (m/e = 2) and CO (m/e = 28) are uncorrected, but the profiles for CH_4 (m/e = 15) are corrected for both ethanol and mercaptoethanol desorption. (b) Coverage dependence of the desorption profiles for CH_3CH_2OH and mercaptoethanol (m/e = 78). The profiles for ethanol are corrected for mercaptoethanol desorption.

previously observed from both reactions of other thiols[1,3,4] and H_2S[6] on Ni(110). Above 0.4 ML, a primary H_2 desorption peak at 265 K remains with a broad high temperature tail. A broad and weak feature was also observed above 400 K. The overall H_2 yield decreases somewhat above 0.2 ML.

Methane Desorption. Methane is observed for coverages greater than about 0.15 ML. The methane desorption shown in Figure 1a has been corrected for fragmentation of both ethanol and, at high coverages, mercaptoethanol. The contribution to the mass 15 signal from ethanol and/or mercaptoethanol desorption has been subtracted using weighting factors determined from mass spectra obtained in the same apparatus from the pure vapors. Methane desorption is observed near 290 K and does not shift significantly with exposure. The methane yield gradually increases below 0.45 ML, but more slowly than the ethanol yield. The lower temperature peaks (below 200 K) at high coverages are associated with either small amounts of impurities in the dosing vapor or to low temperature decomposition in the chemisorbed mercaptoethanol, perhaps at defects. The data shown in the figure were obtained by monitoring the mass 15 signal, but in some experiments the mass 16 signal was also monitored. The mass 15 and mass 16 desorption profiles were both consistent with methane desorption, confirming that the product monitored was neither methyl radicals nor cracking fragments of some other species.

CO Desorption. For low exposures of mercaptoethanol, CO desorbs in a peak at 440 K. This is similar to the desorption temperature for CO itself on clean Ni(110)[21] and is attributed to a desorption limited process. The CO peak below 150 K was not carefully characterized since it was not entirely reproducible but most likely originates from either desorption from the heater leads or the edges of the crystal, since CO formed on the surface would not desorb at such a low temperature, especially at low mercaptoethanol coverages. At coverages above 0.3 ML, the CO desorption yield decreases substantially while the desorption profiles, measured at m/e = 28, become quite complex. The additional structure in the m/e = 28 desorption profiles between 200 and 300 K is at least partially due to desorption of ethanol and acetaldehyde. However, CO desorption at low temperature on Ni(110) has also been observed when preadsorbed oxygen is present.[22] It is very difficult to deconvolute the mass 28 desorption signals; therefore, no corrections for fragmentation of other species have been made, and no attempt was made to interpret the coverage dependence of the integrated desorption yield. However, qualitatively, it is clear that the overall CO desorption yield decreases substantially at high coverage.

Ethanol Desorption. Ethanol desorption was observed for coverages greater than 0.19 ML as seen in Figure 1b. The ethanol was initially observed in two peaks at 240 and 290 K.

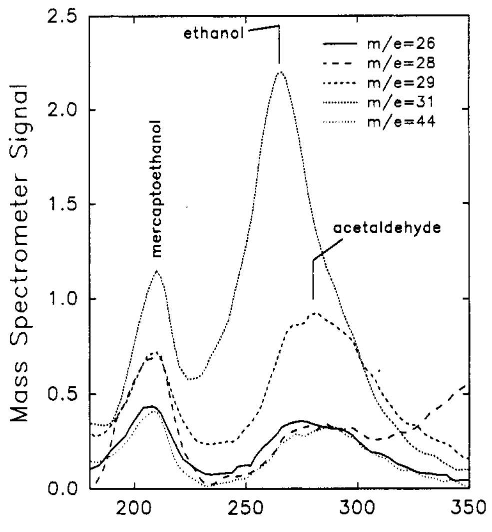

Figure 2. Desorption spectra showing formation of ethanol and acetaldehyde. The curves for mass 26, 28, and 29 are corrected for ethanol desorption to help distinguish the acetaldehyde desorption. The profiles at mass 31 (ethanol only) and 44 (acetaldehyde only) are uncorrected.

With increasing coverage, the low temperature peak dominates and shifts to 265 K. At the highest coverages, a single peak is observed near 265 K. The two peaks observed at lower coverage are attributed to either molecularly bound ethanol or recombination of ethoxide with surface hydrogen. In either case, the C−S bond scission occurred below 240 K. The ethanol desorption spectra look quite reminiscent of both ethanol desorbed from Ni(110) (Figure 7 below) and methanol desorbed from clean or oxidized Ni(110).[8,9] At higher coverages the ethanol peak shifts to 265 K and is associated with ethanol desorption limited by C−S bond scission, which occurs at higher temperature at high coverage. The passivation of the Ni(110) surface toward C−S bond cleavage by S, O, or thiolates has been observed previously.[1,3]

The ethanol was usually monitored at *m/e* = 31, which is also the most intense peak for methanol. However, *m/e* = 45 was sometimes monitored as well, and the signals from masses 31 and 45 were superimposable when scaled appropriately on the basis of reference ethanol mass spectra, suggesting no methanol desorption. The data shown in Figure 1b was corrected at high coverages (>0.40 ML) for desorption of physisorbed mercaptoethanol by subtracting the appropriately weighted mercaptoethanol desorption spectrum.

Mercaptoethanol Desorption. Molecular mercaptoethanol is observed (Figure 1b) for coverages greater than about 0.4 ML, the coverage where the other products saturate. With increasing exposure three peaks are observed and attributed to physisorbed mercaptoethanol, the first at 205 K, the second at 190 K, and the last at 195 K. The 195 K peak does not saturate with increasing exposure and is associated with the thick multilayer. The other peaks, both of which saturate, are associated with desorption of the first several layers of physisorbed mercaptoethanol. Similar structure in the multilayer desorption spectra has been observed for benzene desorption on a variety of surfaces.[23,24]

Acetaldehyde Desorption. Acetaldehyde desorption was observed at 287 K as shown in Figure 2. The primary evidence for this is the desorption peak at mass 44 and the peak asymmetries in the desorption spectra observed at mass 26, 28, and 29. The latter three masses are characteristic of a variety of products including the C_2 hydrocarbons and ethanol. Demonstrating the presence (or absence) of acetaldehyde and C_2 hydrocarbons is important for elucidating mechanistic details of the reaction scheme, despite the relatively small amounts of these compounds observed in the desorption spectra. The desorption spectra shown in Figure 2 are corrected for the contributions from ethanol desorption (based on subtracting the mass 31 spectrum weighted according to mass spectra of authentic ethanol samples), and the desorption state near 285 K due to acetaldehyde is quite clear. The relative intensities in the peak at 285 K are similar to literature reference spectra of acetaldehyde.[25] Essentially all of the features for masses 26, 28, and 29 between 200 and 300 K can be correlated to either ethanol desorption which peaks at 265 K or acetaldehyde desorption which peaks at 285 K. Therefore, there is no compelling evidence for substantial C_2 hydrocarbon production.

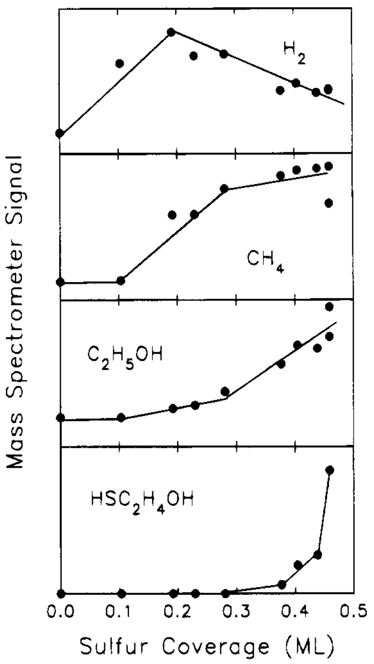

Figure 3. Qualitative coverage dependence of the hydrogen, methane, ethanol and mercaptoethanol desorption yields. Similar data are not shown for acetaldehyde because the amounts are quite small or for CO, since the spectra measured at *m/e* = 28 are complicated superpositions of several different desorption species. Methane and ethanol spectra are offset from the abscissa for clarity.

Although difficult to quantify because of overlapping mass spectral fragmentation patterns, a summary of the reaction coverage dependence of the desorption yields of the hydrogen, methane, ethanol, and mercaptoethanol is shown in Figure 3. The hydrogen yield initially increases to about 0.2 ML and then decreases somewhat. Methane and ethanol are first observed near 0.15 ML and increase with further exposure. The methane signal initially rises with the ethanol yield but saturates at a lower coverage. Molecular mercaptoethanol is observed once the other products have saturated, when the first chemisorbed monolayer is complete.

Desorption Products from Ethanedithiol. Desorption spectra following adsorption of ethanedithiol were measured for comparison to the mercaptoethanol data described above. The saturation coverage of sulfur following a multilayer exposure was 0.6 ML, considerably higher than the 0.45 ML determined for mercaptoethanol. In addition, the desorption data, as shown in Figure 4, indicate a very high selectivity to ethylene formation near 270 K. Only very small amounts of ethane are observed, even when the surface is presaturated with hydrogen. Methane is not a significant desorption product.

XPS Results. X-ray photoelectron spectra were obtained as a function of annealing temperature for the S 2p, C 1s, and O 1s core levels and are shown in Figure 5 for an exposure to

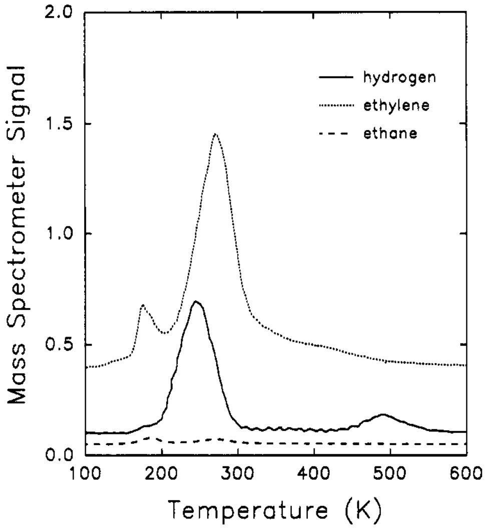

Figure 4. Reaction products observed following a high coverage exposure of ethanedithiol on an initially clean Ni(110) surface.

mercaptoethanol sufficient to produce roughly twice the monolayer saturation coverage. The C 1s, O 1s, and S 2p core level binding energies are given in Table 1. The S 2p core level indicates three distinct forms of S. The first, due to physisorbed mercaptoethanol, is present below 200 K and has a binding energy of 164.0 eV. A second form of sulfur has a binding energy of 163.4 and is stable to about 200 K. This is assigned to a thiolate type intermediate by analogy with methanethiol, benzenethiol and ethanethiol on Ni(110).[1,3,4] In Figure 5, spectrum 1a is comprised of roughly 40% physisorbed mercaptoethanol and 60% thiolate, based on a comparison of the intensity of spectrum 1a with 1b which is due almost entirely to the thiolate species. Annealing for 60 s at 250 K, a temperature on the leading edge of the ethanol desorption, causes a shift to 162.8 eV and a peak which results from a superposition of thiolate and chemisorbed sulfur. Annealing at 300 K (not shown) or above (spectrum 1d) results in a peak at 162.2 eV, which is attributed to chemisorbed sulfur.

The carbon and oxygen XPS spectra as a function of annealing temperature are also shown in Figure 5. Unlike the S 2p photoemission which shows a 0.6 eV shift on desorption of the physisorbed mercaptoethanol, only small shifts of 0.1 eV are observed in the C 1s and the O 1s core levels. Annealing the surfaces at 250 K for 60 s results in mainly a diminution in the peak intensities and a broadening of the peaks. Annealing to 300 K, results in the formation of more clearly defined shoulders on both the C and O spectra. Annealing to 575 K resulted in the complete loss of the C and O signals.

C 1s and S 2p photoemission data were also obtained for ethanedithiol and are summarized in Table 1. The S 2p binding energy for multilayer ethanedithiol is 164.2 eV, equivalent within the precision of the experiment to the value of 164.0 eV obtained for mercaptoethanol. Upon annealing at 170 K to remove the multilayer, a shift to 163.6 eV is observed, consistent with thiolate formation. Essentially all of the sulfur intensity is accounted for by thiolate and some atomic sulfur, suggesting that the molecule is adsorbed as a dithiolate and not as a monodentate species. The monodentate species would have half of the sulfur present as SH groups which would have binding energies like that of the physisorbed thiols.[26]

HREELS Results. Vibrational spectra were measured at both low and high coverage as a function of temperature. The most important qualitative aspects of the spectra were observed for intermediate and high coverages. The data shown in Figure 6 are for an exposure which resulted in about 0.12 ML of sulfur following reaction. A peak at 600 cm^{-1} is observed and attributed to the C$-$S stretching mode. Only weak modes between 1000 and 1800 cm^{-1} are observed, and they are assigned to the C$-$O stretching mode (1015 cm^{-1}) and C$-$C, C$-$H modes which are not resolved. A C-H stretching mode at 2945 cm^{-1} is observed. The CO stretching mode observed at 1862 cm^{-1} is consistent with some initial decomposition, even at low temperature, although some CO is probably adsorbed from the ambient as well. A broad, weak mode at 3300$-$3400 cm^{-1} is observed at high coverage (not shown) and is due to the O$-$H stretching frequency. In spectra of physisorbed mercaptoethanol a mode is observed at 2360 cm^{-1} and is assigned to the S$-$H stretch. The absence of this mode in the chemisorbed layer suggests facile cleavage of the sulfhydryl bond as has been observed on Ni surfaces for simple thiols previously[1-5,12,24] and was suggested by the S 2p XPS data.

Annealing to 250 K results in a dramatic change in the vibrational modes. The spectrum is dominated by a CO stretching mode at 1910 cm^{-1} and by two sharp modes at 885 and 1040 cm^{-1} which are observed at all coverages. The C$-$S stretching mode is missing which indicates that the C$-$S bond is cleaved by annealing to 250 K for 60 s, in agreement with the XPS data. The sharp mode at 1040 cm^{-1} is assigned to the asymmetric C$-$C$-$O stretching mode in an ethoxide species which involves primarily C$-$O stretching. The 885 cm^{-1} mode is assigned to a symmetric C$-$C$-$O stretching mode which is primarily C$-$C stretching in character. Additional modes near 1450 cm^{-1} are assigned to methyl and methylene deformations, and the C$-$H stretching modes are observed at 2995 cm^{-1}. Further annealing to 300 K, a temperature sufficient to remove all ethanol and methane leaves CO on the surface as indicated by the C$-$O stretch at 1942 cm^{-1} and the Ni$-$CO stretch at 411 cm^{-1}. A small peak due to C$-$H stretching modes at 2982 cm^{-1} is present and is associated with an unidentified hydrocarbon species. The decomposition of this species is presumably responsible for the high temperature portions of the hydrogen desorption profile.

Discussion

Adsorption Configuration and Reaction Intermediates. A first clue of the adsorption configuration comes from the saturation coverages of mercaptoethanol and ethanedithiol. The saturation coverage of sulfur obtained following mercaptoethanol adsorption was 0.45 ML, which is similar to that obtained for methanethiol and benzenethiol on Ni(110) but somewhat lower than the 0.55$-$0.65 ML obtained for low temperature adsorption of H_2S on Ni(110).[6] The saturation coverage indicates that steric effects involving the organic moiety preclude reaching the highest sulfur coverages. That mercaptoethanol achieves a coverage comparable to benzenethiol and methanethiol on Ni(110) indicates that the molecule is primarily adsorbed through the sulfur, and not in a bidentate fashion at least at high coverages. If the molecule were adsorbed in a bidentate orientation, or as a mixture of O and S bound species, the saturation sulfur coverage would be expected to be lower since some adsorption sites would be occupied by the oxygen end of the molecule. Similar arguments lead to the opposite conclusion for ethanedithiol where the saturation sulfur coverage is 0.6 ML, higher than observed for any of the simple thiols. This high coverage suggests that sulfur from both ends of the molecule becomes irreversibly adsorbed. A bidentate configuration is proposed for ethanedithiol which is consistent with the very high selectivity toward ethylene formation observed in the TPR and with the XPS data.

Further evidence for the formation of the monodentate β-hydroxy thiolate from mercaptoethanol at high coverage comes from S core level XPS. The S core level shifts 0.6 eV

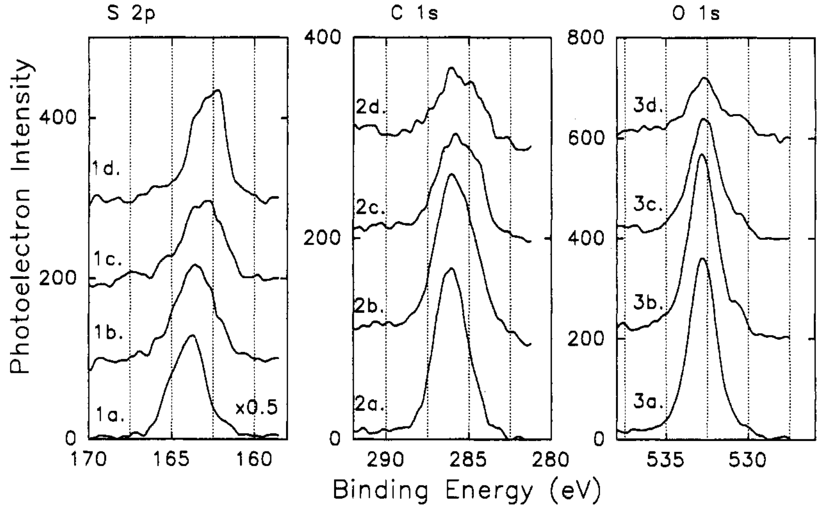

Figure 5. The X-ray photoelectron spectra of the S 2p, O 1s, and C 1s core levels upon adsorption of mercaptoethanol at 100 K (1a, 2a, 3a) and annealing to 200 K (1b, 2b, 3b), 250 K (1c, 2c, 3c), 300 K (2d, 3d), and 600 K (1d).

TABLE 1: XPS Binding Energies (eV)

	T(K)	S $2p_{3/2}$	O 1s	C 1s
mercaptoethanol	100	164.0	532.8	285.9
β-hydroxyethyl thiolate	200	163.4	532.7	285.9
S + ethoxide	250	162.8	532.7	285.8
CO + S + ethoxide	300	162.2	532.7	286, 284.8
S	800	162.2		
ethanol	100		532.5	286
ethoxide	240		532.2	285.5
ethanethiol		164.0		285.5
ethyl thiolate		163.3		284.9
ethanedithiol	100	164.2		
dithiolate	170	163.6		

when the physisorbed mercaptoethanol is desorbed. This type of shift and the binding energies observed for the thiol and the thiolate are entirely consistent with the formation of a thiolate species. For example, as indicated in Table 1, the S 2p binding energies for physisorbed ethanethiol and ethanedithiol are 164.0 and 164.2 eV, respectively, while for the corresponding thiolates the binding energies are 163.3 and 163.5 eV, respectively. It is difficult to determine the extent of interaction between the hydroxyl group and the surface on the basis of the XPS, since the measured O 1s binding energies for ethanol and ethoxide on Ni(110) are nearly equal. The O 1s core level binding energy for roughly 1 ML of physisorbed ethanol (prepared by exposing a heavily sulfided surface to ethanol at 90 K) is 532.5 eV while the binding energy for the ethoxide (prepared by annealing an ethanol overlayer on an initially clean surface to 240 K) is 532.2 eV. The O 1s binding energy following mercaptoethanol exposure changes little with annealing temperature, even when the HREELS strongly indicates the presence of an ethoxide. However, on the basis of the ethanol spectra, little change is expected in the O 1s core level binding energy. The S core level binding energies and shifts observed in the XPS data clearly indicate that the interaction of the sulfur with the surface is strong, but the comparison of the O 1s core level XPS to that of ethanol/ethoxide indicates that the XPS data were insensitive to the interactions between the surface and the hydroxyl group. For this reason, it is impossible to determine the nature of the interaction between the surface and the hydroxyl group.

Upon annealing to 250 K, β-hydroxyethyl thiolate undergoes C—S bond scission and produces both gas phase ethanol and surface ethoxide. The presence of the surface ethoxide is very clear from the HREELS data. At 250 K, the C—S stretching mode is absent, in agreement with the XPS which indicates that C—S bond scission is essentially complete. The most intense modes are the C—O stretching mode at 1040 cm^{-1} and the C—C stretching mode at 885 cm^{-1}. This spectrum is quite similar to that observed by Davis et al. for ethoxide on Pd(111).[27] The growth of the C—O stretch from carbon monoxide is evidence that further reaction has proceeded by 250 K.

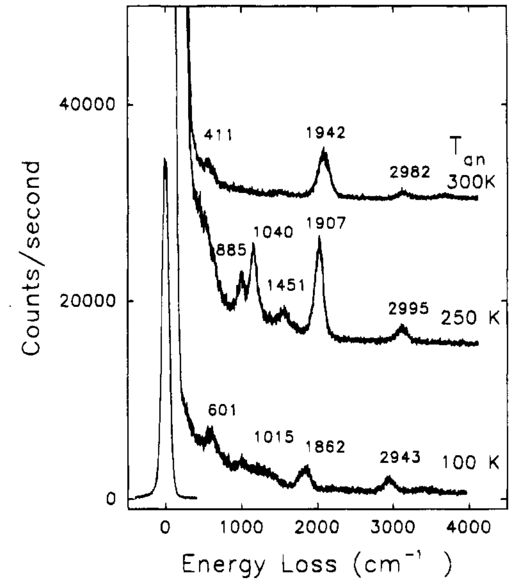

Figure 6. Vibrational spectra measured after annealing a 0.12 ML exposure of mercaptoethanol to the indicated temperatures for 60 s.

The identification of the ethoxide intermediate after annealing to 250 K is based on the HREELS and TPR. The assignment is confirmed by a comparison of the desorption spectra obtained following ethanol and mercaptoethanol adsorptions. The similarity of the methane, hydrogen, and CO desorption spectra shown in Figure 7 provides compelling evidence for a common intermediate in the decomposition pathways of ethanol and mercaptoethanol. The small differences in the desorption temperatures and peak shapes between mercaptoethanol and ethanol in Figure 7 are attributed to the effects of the coadsorbed sulfur in the mercaptoethanol case. The decomposition of ethoxide on Ni(110) is very similar to what has been previously observed for ethanol adsorbed on Ni(111)[11] where the presence of ethoxide was also established spectroscopically. The mercaptoethanol coverage was about 0.2 ML and was chosen for comparison with the ethanol spectra because at higher coverages, ethanol desorption competes with ethoxide formation.

The TPR results are entirely consistent with the spectroscopic identification of the β-hydroxyethyl thiolate and surface ethox-

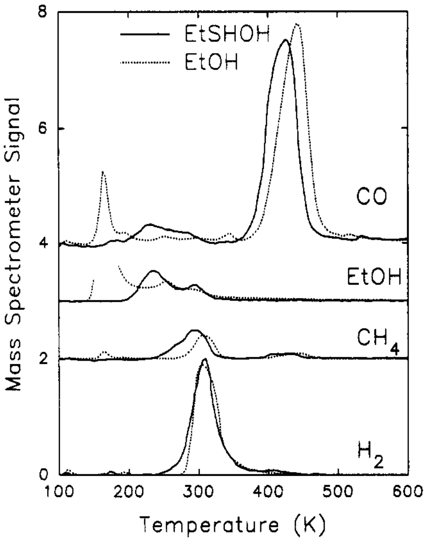

Figure 7. Comparison of the desorption profiles of CO, ethanol, methane, and hydrogen from mercaptoethanol and ethanol adsorption at 100 K. The coverage of mercaptoethanol was about 0.2 ML.

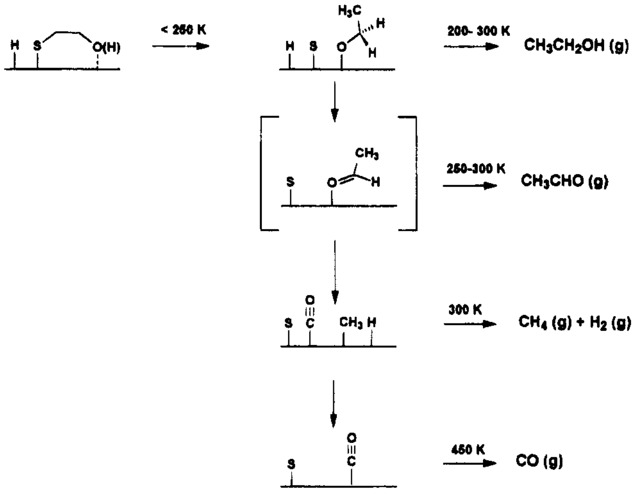

Figure 8. Proposed reaction mechanism for the reaction of mercaptoethanol on the Ni(110) surface.

ide. The presence of acetaldehyde was not confirmed spectroscopically but is clearly formed based on the desorption data.

Reaction Mechanism. Figure 8 illustrates the proposed mechanism of the reaction of mercaptoethanol at high coverage on the Ni(110) surface.

The sulfhydryl bond is cleaved below 100 K, resulting in the formation of the β-hydroxyethyl thiolate. When the C$-$S bond breaks, both gas phase ethanol and surface ethoxide are observed. The ethoxide is then dehydrogenated at the α carbon to form an acetaldehyde intermediate which is not observed spectroscopically but is observed in the desorption. The C$-$C bond cleaves next, leaving CO and methyl groups which are rapidly hydrogenated on this surface.

Qualitatively, the coverage dependence of the desorption yields (Figure 3) can be understood by this mechanism. Ethanol production competes with formation of CO, methane, and hydrogen. The hydrogen is produced both by nonselective decomposition (at low coverages) and from the selective decomposition of the ethoxide to methane, CO, and hydrogen at high coverages. The initial increase in the hydrogen yield is simply a reflection of the initial uptake, but at 0.2 ML, ethanol production begins to become significant, resulting in a decrease in the hydrogen yield. However, since ethoxide is also formed and subsequently produces hydrogen, some hydrogen desorbs at all coverages. The methane yield is flat compared to the ethanol yield for similar reasons. At low coverages, nonselective decomposition dominates and methane is not a significant product. However, as the coverage increases, selective decomposition of ethoxide to methane, CO, and hydrogen is preferred, but ethoxide, and hence methane, formation only occurs in competition with ethanol desorption.

The primary adsorption as a thiolate species can be readily understood when the adsorption energies and dissociation barriers of ethanol and ethanethiol are compared. A bond order conservation model developed by Shustorovich[28] was used to provide values for the chemisorption energies of various chemisorbed species as well as activation barriers for specific reaction steps. When compared to experiment where possible, this method seems to provide reliable predictions. Bell and Shustorovich have previously published both chemisorption energies and reaction barriers for the ethanol system on Ni(111).[16] Those values are used here, and the same procedures were used to calculate the corresponding energies for the analogous sulfur molecules. The only additional parameters required for calculating the energetics of the organosulfur molecules are the carbon-sulfur bond dissociation energies which were taken from the literature.[29,30]

The chemisorption energy of ethanol has been previously calculated as 18 kcal/mole.[16] Using the same method, and assuming a C$-$S bond strength of 72 kcal/mol,[29] the chemisorption energy of ethanethiol is estimated to be 20 kcal/mol. Ethoxide and ethyl thiolate also have similar calculated adsorption energies of 64 and 67 kcal/mol, respectively. This might seem to imply that the bonding interactions between the surface and either the hydroxyl group or sulfhydryl group are essentially the same. However, there is a major difference in the barriers to dissociation of the X$-$H (X = O, S) bond. The estimated barrier to dissociation for chemisorbed ethanethiol to ethyl thiolate is 7 kcal/mol while for the conversion of ethanol to ethoxide the estimated barrier is nearly twice as large, 13 kcal/mol.[16] This effect is also experimetally apparent when comparing the chemisorption behavior of alcohols and thiols on Ni surfaces. Ethanol is observed experimentally to adsorb molecularly at 100 K on Ni(111) and form ethoxide in the temperature range 165$-$200 K.[10,11] In contrast, except for the gold surface,[31] thiols universally undergo S$-$H bond scission at low temperatures, frequently below 100 K.[1-5,32-35] Therefore, if mercaptoethanol adsorbed through the oxygen atom, it would likely be molecularly adsorbed at 100 K, and the interaction would be energetically less favorable than if it adsorbed through the sulfur atom with dissociation of the S$-$H bond. The mercaptoethanol molecule is flexible enough that even if the molecule were bonded as an chemisorbed alcohol initially, the sulfhydryl group could still access the surface and form the thiolate intermediate.

The formation and subsequent reactions of ethoxide and the β-hydroxyethyl thiolate in this system allow some interesting comparisons to be made between the two species. While the thiolate reacts via C$-$S bond scission to produce ethanol, essentially no C$-$O bond scission is observed. This is partly a reflection of the difference in bond energies between C$-$O and C$-$S bonds. Reaction barriers and adsorption energies calculated using the BOC-MP method for ethoxide[16] and ethyl thiolate are shown in Table 2. In the case of ethoxide, the barrier to dissociation of the C$-$X bond is estimated to be 13 kcal/mol as compared to 6 kcal/mol for the thiolate. Within the context of the BOC-MP method, the biggest contribution to that difference is the C$-$X bond strength. It is interesting to note that for ethoxide the loss of the methylene hydrogen to form adsorbed acetaldehyde is predicted to be kinetically preferred (barrier to dehydrogenation of 7 kcal/mol vs 13 kcal/mol for

TABLE 2:

(a) Calculated[a] Adsorption Parameters

	$Q^{\ddagger}$ [d]
ethanethiol[b]	20
ethyl thiolate	67
"thioacetaldehyde"	23
ethanol[c]	18
ethoxide[c]	64
acetaldehyde[c]	19
ethyl[c]	64
S	112
O	115
H	63

(b) Activation Energies for Surface Reactions

reaction step	E* [d]
$CH_3CH_2SH \rightarrow CH_3CH_2S + H$	7
$CH_3CH_2S \rightarrow CH_3CH_2 + S$	6
$CH_3CH_2S \rightarrow CH_3CH\ S + H$	23
$CH_3CH_2OH \rightarrow CH_3CH_2O + H$	13
$CH_3CH_2O \rightarrow CH_3CH_2 + O$	13
$CH_3CH_2O \rightarrow CH_3CHO$	7

[a] BOC-MP method, ref 28. [b] Assuming $D_{C-S} = 74$ kcal/mol and $D_{C=S} = 130$ kcal/mol. [c] Reference 16. [d] $Q^{\neq}$ = adsorption energy (kcal/mol), E^* = activation energy (kcal/mol).

C−O bond scission[16]) and is in fact observed in this study and in the study of ethanol decomposition itself on Ni(111).[10,11] Once the acetaldehyde intermediate has been formed, the subsequent loss of the other methylene hydrogen and C−C bond scission are expected. Analogous reaction barriers and chemisorption energies involving dehydrogenation of the thiolate were also estimated, and assuming a C=S energy of about 130 kcal/mol,[30] the adsorption energy of "thioacetaldehyde", CH_3CHS, is about 23 kcal/mol and the barrier to formation of thioacetaldehyde from ethyl thiolate is about 30 kcal/mol, much larger than the 6 kcal/mol barrier to C−S bond scission.

The proposed reaction pathway for mercaptoethanol is entirely consistent with the estimated bonding parameters. First, the molecule is strongly bound through the sulfur atom with dissociation of the sulfhydryl bond. Second, C−S bond scission is preferred to C−H or C−O bond scission and results in formation of both gas phase ethanol and surface ethoxide. In the ethoxide, scission of the methylene C−H bond is preferred to C−O bond scission, resulting in formation of acetaldehyde. This reaction sequence is essentially controlled by the relative strengths of the carbon−oxygen and carbon−sulfur single and double bonds.

In contrast, ethanedithiol does not react in the analogous stepwise fashion to produce ethanethiol, ethyl thiolate, and surface sulfur. No ethanethiol was observed in the desorption experiment, and the formation of ethyl thiolate is ruled out by the very high selectively toward ethylene formation. Unlike ethanedithiol, ethanethiol on either a clean or sulfided surface produces substantial quantities of ethane as well as ethylene. Ethanedithiol apparently undergoes two essentially simultaneous C−S bond scission steps to split out ethylene. The comparison of the reactivity of ethanedithiol with that of mercaptoethanol suggests that the reaction pathways are, in fact, controlled largely by the bond energetics and not by steric factors.

Conclusion

The reaction pathways for mercaptoethanol on Ni(110) have been determined and compared to ethanedithiol, ethanol, and ethanethiol. Mercaptoethanol reacts by formation of a β-hydroxyethyl thiolate at low temperature. Carbon−sulfur bond scission occurs near 250 K, resulting in the desorption of ethanol and the formation of surface ethoxide. The ethoxide undergoes C−H bond scission to form acetaldehyde and eventually methane and carbon monoxide. The identity of the surface species was determined by a combination of X-ray photoelectron spectroscopy, high resolution electron energy loss spectroscopy, and reaction product distributions. In contrast, ethanedithiol forms a bidentate ethyl dithiolate which splits out ethylene with very high selectivity. These reaction pathways are to a large extent controlled by the relative strengths of the C−S, C−O, O−H, and S−H bonds. The results of this study correlate with the observation that hydrodesulfurization (HDS) catalysis is usually more facile than hydrodeoxygenation (HDO).

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