

Benzenethiol Reaction on the Clean and Hydrogen Pretreated Ni(100) Surface

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Benzenethiol reactions on clean and hydrogen precovered Ni(100) surfaces have been studied in order to characterize C–S bond breaking. Benzenethiol adsorbs at 90 K as phenylthiolate and surface hydrogen. The dominant benzene formation pathway for large coverages of benzenethiol occurs at 270 K. C–S bond breaking involves direct reaction of phenylthiolate with the nickel surface; hydrogen does not appear to be directly involved. The rate-limiting C–S bond breaking step is followed by rapid hydrogenation of adsorbed phenyl to form benzene which desorbs from the sulfur covered surface. Deuterium incorporation studies support this mechanism since single hydrogen addition dominates as expected for hydrogenation of an adsorbed phenyl intermediate. For the benzenethiol saturated surface (0.30 monolayer), hydrogen preadsorption increases the temperature for benzene formation by up to 20 K and increases the benzene yield up to 37%. Reorientation of the phenylthiolate away from the surface in the presence of large coadsorbed hydrogen coverages is indicated by vibrational characterization. This hydrogen induced reorientation appears to be associated with the increase in C–S bond activation energy. Above 500 K dehydrogenation of adsorbed phenylthiolate derived species results in formation of surface bound polyaromatic hydrocarbons (PAHs) coadsorbed with sulfur; the hydrogen formed in this process desorbs. For low coverages of benzenethiol, no 270 K benzene is observed due to increased dehydrogenation by the surface. A small amount of benzene is formed by disproportionation above the temperature of free hydrogen desorption (400 K). A comparison of benzenethiol reactions on the three low Miller index surfaces of nickel clearly indicates that hydrogen availability at reaction temperature has a large influence on benzene formation. Hydrogen desorption prior to C–S bond activation on the Ni(100) surface limits benzene formation, while substantial hydrogen availability on the Ni(111) and Ni(110) surfaces facilitates benzene formation.

Introduction

Desulfurization is an industrially important reaction that has been studied by a variety of methods.^{1–11} Adsorption and reaction of organic thiols has been characterized on several single-crystal metal surfaces as part of efforts to improve our understanding of the surface processes involved in hydrosulfurization reactions. The research described in this paper is focused on the reactions of benzenethiol on the Ni(100) surface. By combining reactivity and spectroscopic studies, the mechanisms for benzenethiol disproportionation, hydrogenation, and dehydrogenation have been examined. Special emphasis has been placed on potential involvement of hydrogen in C–S bond scission and other important reaction pathways. Finally, benzenethiol reactions on the Ni(100) surface will be compared with analogous reactions on the Ni(111) and Ni(110) surfaces so that correlations between reactivity and surface structure can be developed.

Benzenethiol has been studied on the Mo(110),¹² Cu(110),¹³ Rh(111),¹⁴ Ni(110),¹⁵ Ni(100),¹⁶ and Ni(111)^{17,18} surfaces using a range of ultrahigh vacuum methods. On each of these surfaces, the benzenethiol is adsorbed through the S atom with cleavage of the S–H bond, producing surface thiolate and surface hydrogen at low temperature. The aromatic ring is typically found to be oriented either perpendicular or nearly

perpendicular to the surface. On Mo(110),¹² NEXAFS studies indicate a tilt of 23° away from surface normal, while on Pt(111)¹⁹ and Ag(111)²⁰ electrodes the aromatic ring was found to be perpendicular to the surface by HREELS.

The desulfurization of benzenethiol has previously been studied on the Mo(110),¹² Ni(110),¹⁵ and Ni(111)^{17,18} surfaces. Thermal disproportionation of benzenethiol on Mo(110) leads to benzene desorption at 350 K, attributed to a slow hydrogenolysis of the C–S bond followed by fast desorption. Dehydrogenation at high temperatures results in formation of surface benzyne, which is stable on the sulfur modified Mo(110) surface up to 680 K. With further increases in temperature, dehydrogenation results in desorption of hydrogen and formation of surface carbon. On the Ni(110) surface, benzenethiol forms benzene at approximately 220 K by reaction of the surface thiolate with free hydrogen formed during thiolate formation. Additional benzene peaks are observed at high temperature from disproportionation in the absence of coadsorbed hydrogen. On the Ni(111) surface, benzenethiol forms benzene at 260 K by reaction of the thiolate in the presence of free coadsorbed hydrogen. Benzene formation also occurs at 290 K by hydrogenation of a benzyne group oriented perpendicular to the surface in the presence of free coadsorbed hydrogen. An additional benzene peak is observed above 350 K from disproportionation of remaining phenylthiolate derived species.

The bond lengths and orientations of phenylthiolate on the Ni(100) surface have been characterized using XANES and

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EXAFS.¹⁶ These methods indicate that, after desorption of the physisorbed layer, a chemisorbed phenylthiolate species remains. The phenylthiolate is located in the 4-fold hollows of the Ni(100) surface and is nearly normal to the surface plane. A series of adsorbed thiols, including methanethiol and alkane-thiols with chain lengths of up to six carbons, have also been characterized on the Ni(100) surface.²¹ For all of these cases, the saturation coverage of thiol was found to be approximately 0.28 monolayer, which was limited by steric factors associated with ordering of the alkyl chains. The hydrogenolysis of methanethiol was studied in some detail with methane formation occurring at 270 K.²² This methane formation peak broadens and shifts slightly to 260 K with hydrogen preexposure.

Recent experiments with coadsorbed methanethiol and benzenethiol have yielded important information about the role of hydrogen in C–S bond activation on nickel surfaces.^{23,24} In addition to the hydrogenolysis products methane and benzene, toluene formation also results from the thermal reaction of the coadsorbed thiols. The toluene formation temperature corresponded exactly with the methane and benzene formation temperatures. Since the addition of the hydrocarbon groups occurs at the same temperature as hydrogen addition, the activation of the C–S bond must limit the rates of both reactions. Therefore direct insertion of Ni in the C–S bond must lead to bond scission without direct involvement of hydrogen. That is, even though hydrogen addition occurs during benzene formation, hydrogen is not involved in the rate-limiting C–S bond breaking step.

Experimental Section

These temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) experiments were performed in a stainless steel ultrahigh vacuum chamber described in detail elsewhere¹⁷ with a base pressure of 1×10^{-10} Torr. This system was also equipped with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and a sputter gun. The Ni(100) samples were mounted on a liquid nitrogen cooled manipulator which could be cooled to 90 K and heated resistively to 1000 K via tungsten support wires. Type E thermocouple wires were spot welded to the back of the crystal for temperature measurement and control.

Temperature programmed desorption experiments were performed using a multiplexed quadrupole mass spectrometer. The mass spectrometer was unshielded, requiring that the sample be biased at -70 V during TPD experiments to prevent electron stimulated desorption or decomposition.¹⁵ During experiments, the sample was placed within 1 cm of the mass spectrometer ionizer. The heating rate used for all TPD experiments was 5 K/s. HREELS data were obtained using a LK2000 EEL spectrometer with an experimental resolution of 4–6 meV.

In all experiments, benzenethiol was purified by several freeze–pump–thaw cycles. The crystal was positioned within 1 mm of a directional doser, and benzenethiol was dosed through a 19 mm laser-drilled aperture to the crystal. The pressure behind the aperture was controlled by placing the benzenethiol in an ice water bath (0 °C). H₂S was dosed via a pressure controlled cell through a separate directional doser and used without further purification. Hydrogen, deuterium, and sputter gases were dosed by back-filling the chamber through a leak valve and were used without further purification. The purity of these gases were confirmed by regular mass spectroscopy checks.

The uptake of benzenethiol was monitored by AES. No sulfur containing species desorb from the surface below mono-

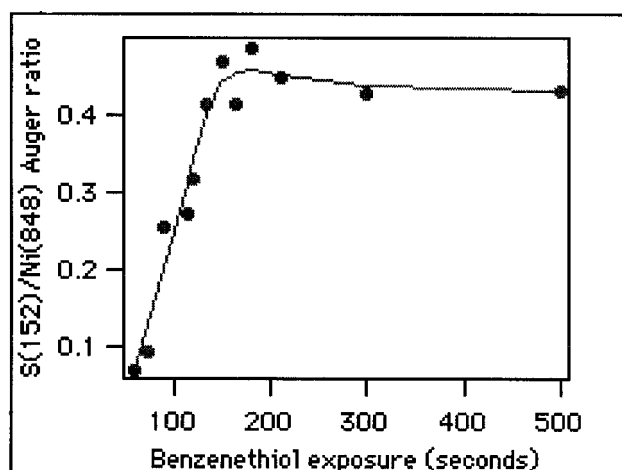


Figure 1. Uptake of benzenethiol on the Ni(100) surface as a function of coverage. The S(152)/Ni(850) Auger peak reactions are plotted against benzenethiol exposure, measured in seconds. The uptake curve plateaus above 185 s of benzenethiol, indicating saturation coverage with a S/Ni peak ratio of 0.45, which represents 0.30 monolayer of benzenethiol.

layer coverages, so that the S(152eV) Auger peak following complete thermal reaction is proportional to the initial coverage of adsorbed benzenethiol.

Results and Discussion

Coverage Determination. To determine the saturation coverage of the benzenethiol, the ratio of the sulfur Auger peak at 152 eV to the nickel Auger signal at 850 eV was first calibrated against an established structure of sulfur with a known sulfur coverage.²⁵ The 0.5 monolayer sulfur saturation at 800 K corresponds to a $c(2 \times 2)$ overlayer structure with a S(152eV)/Ni(850eV) Auger ratio of 0.75. This structure was obtained by repeated exposure to H₂S followed by annealing to 800 K to remove hydrogen. After each exposure and annealing, hydrogen desorption was monitored until no hydrogen desorption was observed, the resultant LEED pattern was examined until a $c(2 \times 2)$ structure formed, and the AES spectrum was taken until no increases in Auger ratio were observed. This structure is well-known and corresponds to sulfur adsorbed in alternate 4-fold hollows on the surface.

Since no sulfur containing species desorb from the surface for thiol coverages below a monolayer, the S(152eV) Auger peak following a high-temperature anneal is proportional to the initial coverage of adsorbed benzenethiol. Figure 1 shows the uptake of sulfur on the Ni(100) surface for a range of benzenethiol exposures which have been heated to 800 K. Saturation is reached at a S(152)/Ni(850) Auger ratio of 0.45 which indicates a saturation coverage of benzenethiol of 0.30 monolayer. This value is in excellent agreement with other thiols on the Ni(100) surface.²¹

Temperature Programmed Desorption Studies. The desorbing products from thermal reaction of 0.30 monolayer saturation coverage of benzenethiol are shown in Figure 2. Benzenethiol multilayers desorb from the surface at 180 K with a small shoulder associated with surface interactions extending up to 200 K. The primary benzene desorption peak appears at 270 K. This primary peak has a substantial leading edge extending down to 200 K, possibly due to multiple reaction processes occurring in this saturated overlayer. The broad hydrogen desorption from benzenethiol dehydrogenation begins near 200 K and extends to near 400 K. Above 600 K, a series of complex hydrogen desorption peaks resulting from dehy-

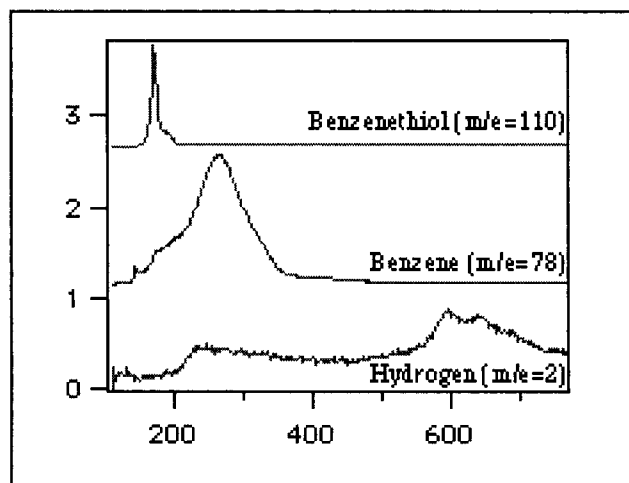


Figure 2. TPD spectra of 0.30 monolayer benzenethiol on the Ni(100) surface. The only products found to desorb are benzene, hydrogen, and molecular benzenethiol. Carbon from decomposition indicated by the hydrogen desorption is believed to absorb into the bulk of the crystal.

drogenation of adsorbed hydrocarbons appear. As mentioned in the Experimental Section, no sulfur containing compounds desorb after the desorption of benzenethiol multilayers. No other species were found to desorb in these experiments.

The effect of increasing the surface coverage of benzenethiol on hydrogen and benzene desorption is illustrated in Figure 3. For low coverages, only a trace of benzene desorption is observed at 475 K, and dehydrogenation clearly dominates with a broad hydrogen desorption feature between 300 and 500 K. As benzenethiol coverage increases, the benzene peak temperature decreases to 420 K, with a gradually increasing peak area. The maximum high-temperature benzene yield occurs at approximately 0.15 monolayer. The dominant benzene formation channel for higher coverages occurs near 270 K with a leading shoulder at 200 K. As the primary benzene peak at 270 K increases with increasing coverage above 0.15 monolayer, the 420 K peak gradually decreases and is difficult to discern for saturation coverages of benzenethiol. The leading shoulder near 200 K decreases relative to the main peak at 270 K with increasing coverage. The 270 K peak grows steadily until saturation of the surface by benzenethiol occurs; however, the leading shoulder is clear even at saturation coverage. The 280 K hydrogen desorption remains very small and approximately constant over the entire range of increasing benzenethiol coverages. The decrease in hydrogen desorption temperature observed is associated with increases in sulfur coverage.

Benzenethiol adsorption on a hydrogen precovered Ni(100) surface was used to study the role of hydrogen in benzene formation. The addition of external hydrogen generally increases the amount of benzene formed for a 0.30 monolayer coverage of benzenethiol, as shown in Figure 4. An increase of 37% in the benzene yield is observed with a 10 langmuirs H_2 preexposure. For the larger hydrogen preexposure of 20 langmuirs, the benzene peak temperature increases by 20 K as hydrogen exposure increases, indicating that C–S bond activation is inhibited by large exposures of coadsorbed hydrogen. On the Ni(111) surface, predosing with hydrogen limited the uptake of benzenethiol;¹⁸ however, a similar effect is not observed here. Since the benzenethiol coverage is the same on the clean and hydrogen predosed Ni(100) surface, the reduction in benzene formation indicates reduced reactivity. As discussed below, this inhibition is correlated with reorientation of the molecule away from the surface. Hydrogen preadsorption

does not affect the high-temperature benzene formation. The loss of the 200 K shoulder at high hydrogen preexposures, coupled with its decrease at higher benzenethiol exposures, demonstrate that the 200 K process is sensitive to surface coadsorbates and coverage. The 180 K shoulder observed in Figure 4 is caused by fragmentation in the mass spectrometer associated with physisorbed benzenethiol and does not represent an additional benzene formation pathway. Preexposure to hydrogen does not have a very large effect on the reactivity of submonolayer coverages on benzenethiol. While small amounts of benzene desorb from the Ni(100) surface at 270 K, the dominant pathway remains high-temperature benzene formation. This is in contrast to distinct increases in reaction selectivity observed with coadsorbed hydrogen for low benzenethiol coverages on the Ni(111) surface.

Figure 5 shows the results of the reaction of 0.30 monolayer of benzenethiol with 10 langmuirs of preadsorbed D_2 . Singly deuterated benzene is the dominant deuterated product, suggesting that addition of a single deuterium (hydrogen) is involved in the primary reaction sequence. No substantial concentrations of multiply deuterated benzene were observed during these experiments. The absence of multiple deuterium incorporation indicates that the thiolate does not exchange rapidly with the surface and that multiple hydrogen addition steps do not occur in the primary reaction pathway. No temperature shift is induced by deuterium incorporation. A large amount of hydrogen from low-temperature thiol dehydrogenation remains adsorbed on the “deuterium saturated” surface, as indicated by the large hydrogen and HD desorption peaks in the upper spectra. Given the large amount of hydrogen present, it is not surprising that a large amount of benzene- d_0 is formed. Reaction of 0.10 langmuir of benzenethiol with 10 langmuirs of D_2 produced a very small amount of low-temperature benzene, with a similar D incorporation pattern (data not shown). The small high-temperature benzene peak was found to form up to benzene- d_4 , indicating a multiple D incorporation into the surface intermediate.

Vibrational Characterization of Surface Intermediates.

The HREELS spectra for multilayer benzenethiol annealed to a series of specific temperatures is shown in Figure 6. At 90 K, the existence of the multilayer is confirmed by the presence of both the 2550 cm^{-1} S–H stretch and the 250 cm^{-1} (τ (S–H)) bend.¹² Heating to 190 K eliminates these features, indicating that only a monolayer of thiolate remains. The vibrational modes associated with the phenyl ring of the benzenethiol will prove valuable to the identification of surface intermediates. The out of plane C–H bend of the ring can be found at approximately 740 cm^{-1} , and the C–H stretch occurs at 3050 cm^{-1} . Additional ring bending and stretching modes occur at about 1000, 1150, and 1500 cm^{-1} . These modes and the surface selection rules provide valuable information about the orientation of molecules on the nickel surface. Off-specular measurements have determined that the out of plane C–H modes are dipole active vibrational modes, while the other modes listed are dipole inactive. This makes the intensity of the vibrations at $\sim 740\text{ cm}^{-1}$ sensitive to the orientation of the phenyl ring relative to the surface plane. Specifically, when the molecule is oriented with the ring parallel to the surface, the intensity of the out of plane bend relative to the ring modes will be much larger than for a phenyl ring oriented away from the surface. Significant features are described in Table 1, along with comparisons to similar systems. The intensity of the dipole active 740 cm^{-1} peak relative to that of the ring modes suggests that the phenylthiolate is adsorbed nearly perpendicular to the

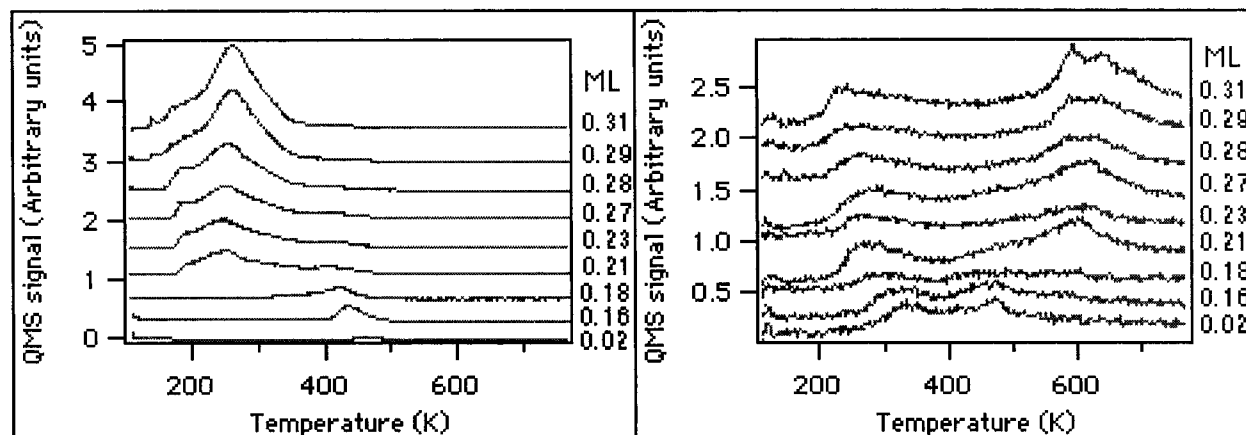


Figure 3. Temperature program desorption profiles for benzene (left) and hydrogen (right). Exposures of benzenethiol are reported in seconds and range from approximately 0.05 monolayer at 60 s to a multilayer coverage at 300 s.

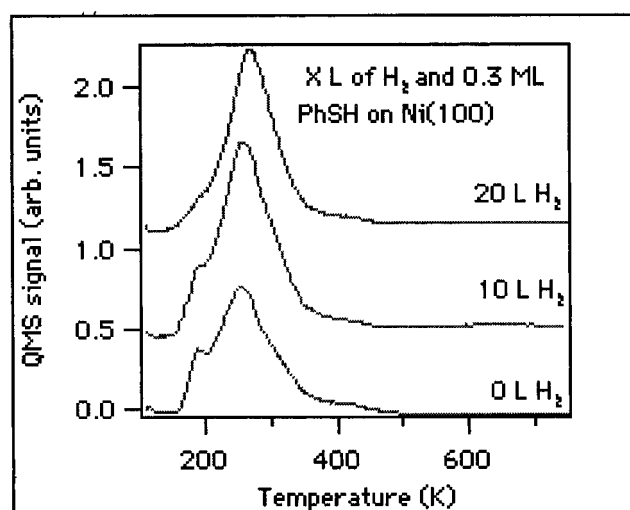


Figure 4. Benzene desorption from monolayer benzenethiol on the clean and hydrogen predosed Ni(100) surface. Hydrogen generally increases benzene formation. Benzene desorption temperature also increases with increasing hydrogen exposure.

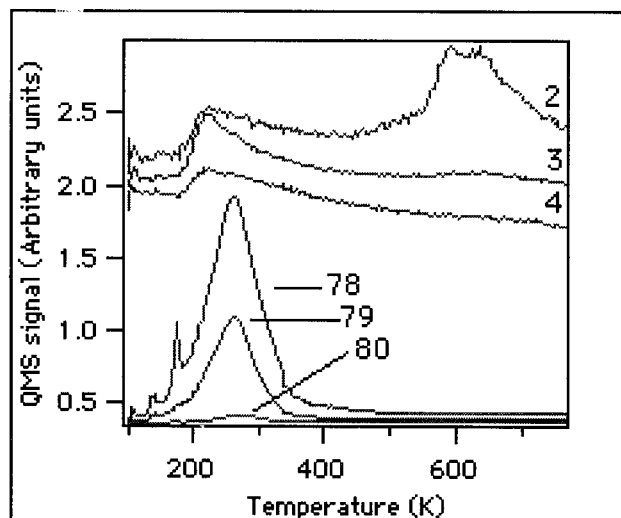


Figure 5. Deuterium incorporation from preadsorption of 10 langmuirs of D₂ followed by 0.30 monolayer benzenethiol. D₁ and d₂ products are observed clearly, while high incorporation occurs only in trace amounts. Labels shown are the *m/e* values for each curve.

surface, supporting XANES work which indicates a nearly perpendicular adsorption geometry.¹⁶ A loss in the 740 cm⁻¹ peak intensity relative to the ring modes is observed when the sample is heated beyond the benzene desorption temperature to 300 K (Figure 6, 300 K). This is attributed to a reorientation of the remaining aromatic species. Comparison of the data to previous experiments^{12,15,18} indicates that the intermediate is a partially dehydrogenated phenyl ring, oriented largely parallel to the surface. New features also begin to form at 300 K, most notably modes at 590 and 1210 cm⁻¹. Heating to 500 K creates a significant increase in these two features and also a shift of the 1470 cm⁻¹ peak to 1550 cm⁻¹. Comparison of the 500 K HREELS spectrum to published IR spectra²⁶ suggests that the surface species is similar to a polyaromatic hydrocarbon like phenanthrene. The strong correlation between the peak positions and intensities to phenanthrene (Table 1), and the reported polymerization of benzene containing species on the Ni(100) surface,^{27,28} is consistent with the condensation of the surface C₆ rings to form polyaromatic hydrocarbon. Upon further heating, the remaining surface hydrocarbon species dehydrogenate and carbon is absorbed into the bulk, with only sulfur remaining on the surface.

Vibrational analysis of small coverages of benzenethiol provides additional information regarding benzene formation

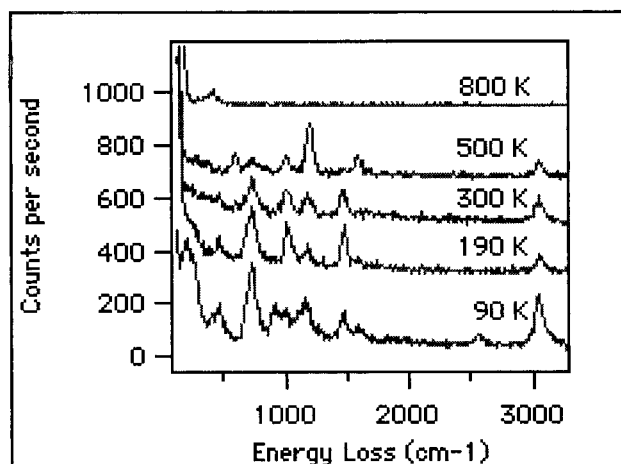


Figure 6. HREELS anneal set for multilayer benzenethiol coverage on the Ni(100) surface. For all temperatures, the crystal was heated to the desired temperature and then cooled to 100 K.

at lower coverage. The vibrational anneal set for 0.10 monolayer of benzenethiol is shown in Figure 7. The vibrational modes are assigned in Table 1. The absence of S-H modes at 2250 cm⁻¹ indicates that thiolate is formed on adsorption at

TABLE 1: Relevant Energy Losses for Benzenethiol on the Ni(100) Surface in Addition to the Multilayer, Submonolayer, and Hydrogen Predosed Multilayer Sets, Reference Spectra of Benzenethiol on Ni(111), and the IR Spectrum of Phenanthrene

assignm ^a	C ₆ H ₅ SH 110 K	C ₆ H ₅ S 190 K	C ₆ H ₅ 300 K	"PAH" 500 K	C ₆ H ₅ S/ Ni(110) ^b	C ₆ H ₅ S/Mo(110) ^c	phenanthrene ^d
$\nu(\text{Ni}-\text{SC}_6\text{H}_5)$	465	450	472		449		
C—C—C bend				590			582.0
$\gamma(\text{C}-\text{H})$	738	738	738	753	743	750	756.2
$\beta(\text{C}-\text{H}) + \nu(\text{C}-\text{C})$	1003	1018	1011	1011	956	1035	
$\gamma(\text{C}-\text{H})$	1166	1188	1188	1210	1185		1277.5/1282.5
$\nu(\text{C}-\text{C})$	1476	1483	1469	1475	1496	1510	
$\nu(\text{C}-\text{C})$							1565.0
$\nu(\text{C}-\text{H})$	3048	3055	3055	3063	3070	3170	

^a ν = stretching mode; γ = out of plane bend; β = in plane bend. ^b Reference 15. ^c Reference 12. ^d Reference 26.

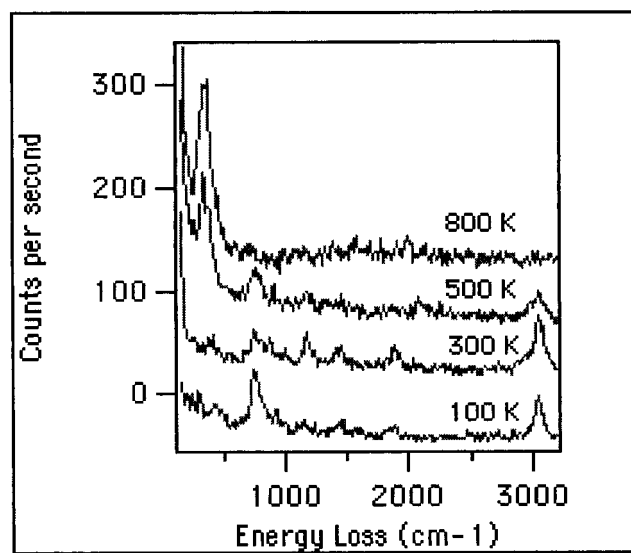


Figure 7. HREELS anneal set for submonolayer (~ 0.05) benzenethiol coverage on the Ni(100) surface. As before, all temperatures shown indicate that the crystal was heated to the desired temperature and then cooled to 100 K. The low coverage produced reduced the total signal, and thus the spectra are not as clear as those for the multilayer. Spectra were smoothed to more clearly resolve the features.

100 K; no molecular benzenethiol remains. The HREELS is somewhat noisy because of small coverage; however, a comparison of the dipole active 740 cm^{-1} C—H bend and the 3050 cm^{-1} C—H stretch indicates that the low-coverage thiolate is adsorbed nearly parallel to the surface. Extensive dehydrogenation observed in low-coverage TPD experiments also supports this conclusion. Extensive interaction with the ring is also supported by the deuterium incorporation data discussed above. Substantial interactions between phenyl groups and metal surfaces results in parallel adsorbed configurations for benzenethiol on other surfaces.^{12,17} Further heating does not produce the polyaromatic hydrocarbons (PAHs) seen for larger coverages.

To further characterize the role of hydrogen in benzenethiol surface reactions, HREELS spectra of coadsorbed hydrogen and high coverages of benzenethiol were taken for the same series of annealing temperatures. A significant difference was observed at 190 K just before C—S bond activation in these TPD experiments. Figure 8 compares the HREELS spectra after annealing to 190 K for benzenethiol and benzenethiol coadsorbed with hydrogen. Previous experiments have shown that the out of plane bending mode at 730 cm^{-1} is dipole active and therefore depends on thiolate orientation, while the 900 cm^{-1} mode is impact scattered and does not depend on thiolate orientation.¹⁸ The significant loss of intensity in the 740 cm^{-1} dipole mode with coadsorbed hydrogen indicates that the ring

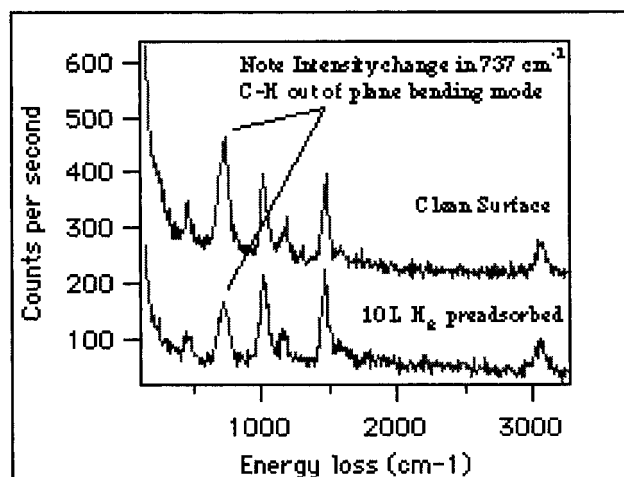


Figure 8. HREELS spectra of 0.30 monolayer of benzenethiol on clean (solid line) and hydrogen predosed (dashed line) surfaces after annealing to 190 K. The preadsorption of hydrogen is found to change the orientation of the phenyl ring relative to the surface, making the ring more perpendicular to the surface.

has reoriented away from the surface toward a more upright orientation. No significant differences were observed between the clean and hydrogen pretreated surfaces at any other annealing temperatures. TPD following large hydrogen exposures in fact shows a decrease in reactivity associated with the reoriented phenylthiolate. The increased activation energy for C—S bond activation is consistent with reorientation of the molecules away from the surface. So, in addition to being a reactant, adsorbed hydrogen also influences reactivity by modification of intermediate adsorption geometry.

Reaction Mechanism. A summary of the primary benzenethiol reaction on the Ni(100) surface is shown in Figure 9. Benzenethiol adsorbs dissociatively to form surface hydrogen and phenylthiolate¹⁶ which adsorbs at 4-fold hollow sites and surface hydrogen at 100 K. The saturation coverage of benzenethiol is 0.30 monolayer, which is similar to the saturation coverage of many similar simple organic thiols.²¹ This result indicates a largely upright adsorption geometry for phenylthiolate, since the aromatic ring would cover substantial surface area in a parallel configuration or tilted configuration for the large saturation coverage observed. An upright orientation is also supported by HREELS data. The initial C—S bond activation step for saturation coverages of benzenethiol involves direct reaction with the metal surface at 270 K. The formation of an adsorbed phenyl intermediate is clearly indicated by toluene formation at the same temperature from coadsorbed methanethiol and benzenethiol.²⁴ Hydrogen is not involved in the rate-limiting C—S bond breaking process. The yield of the singly deuterated benzene product at 270 K indicates that surface hydrogen is involved in the primary reaction path and that

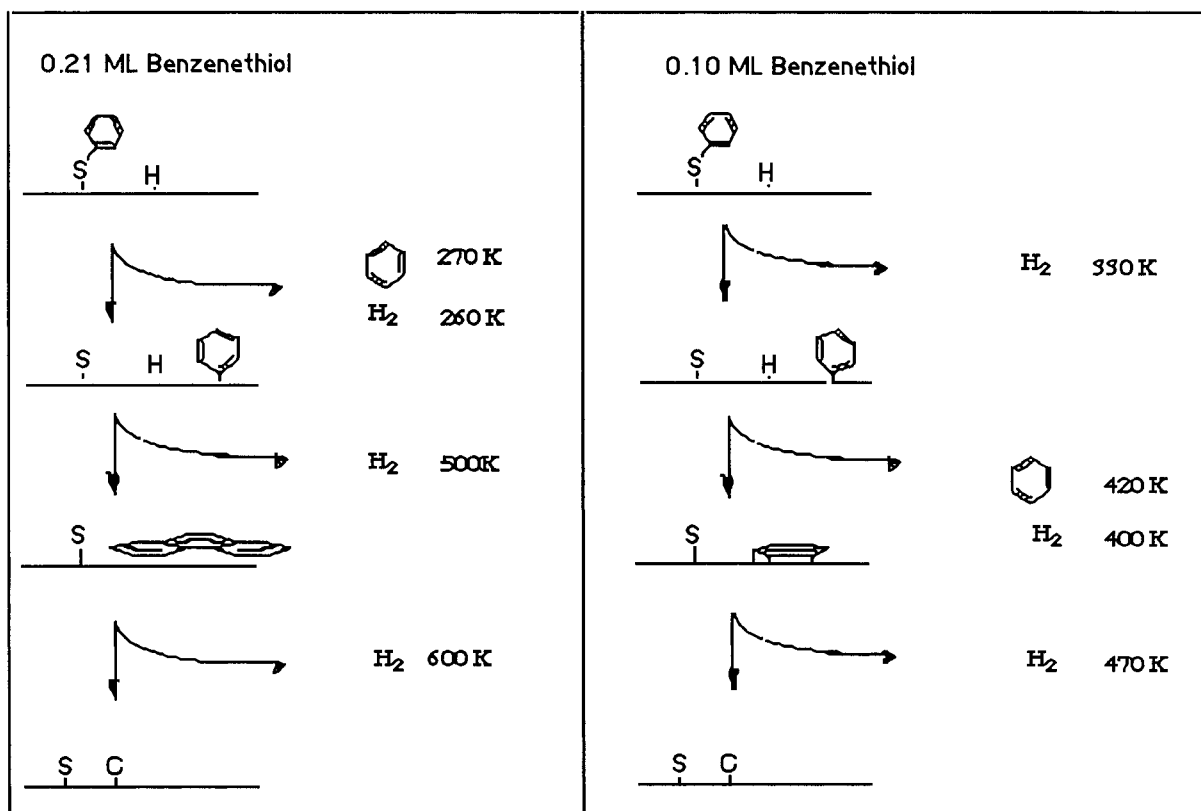


Figure 9. Reaction scheme for the formation of benzene from benzenethiol on the Ni(100) surface (0.03 and 0.10 monolayer coverages).

addition of a single hydrogen is dominant. Temperature programmed reaction of low coverages < 0.1 monolayer of benzenethiol does not result in benzene desorption at 270 K. Benzene desorption does not occur for low coverages until disproportionation begins near 400 K (Figure 2). With increasing amounts of preadsorbed hydrogen up to 10 langmuirs, the yield of benzene increases for large phenylthiolate coverages. Additional hydrogen results in increased hydrogenation and decreased phenyl dehydrogenation. For large hydrogen coverages, reorientation of the phenylthiolate intermediate is demonstrated by vibrational characterization shown in Figure 8. Above a hydrogen preexposure of 20 langmuirs, this reorientation away from the surface results in the inhibition of C–S bond activation as expected since interaction with the α carbon is required for metal catalyzed C–S bond activation. Unreacted phenyl groups on the surface are oriented largely perpendicular to the surface for temperatures up to 500 K (Figure 6). With further increases in temperature dehydrogenation and polyaromatic hydrocarbons, formation is evidenced by the growth of several vibrational modes not attributed to individual phenyl rings (Figure 6 and Table 1). As temperature increases beyond this point, nonselective decomposition dominates until only surface sulfur remains (carbon is absorbed into the bulk of the crystal at this point and is not observed by any of the techniques available). Additionally hydrogen does not influence reaction for the low coverage of benzenethiol. This is due to dominance of dehydrogenation for the parallel adsorbed molecule and the lack of hydrogen availability at reaction temperature.

Comparison of Benzenethiol Reactions on Low-Index Ni Surfaces. The surface reactions of benzenethiol have been characterized at a molecular level on all three low Miller index nickel surfaces. The paragraphs which follow summarize the primary reactions observed for benzenethiol on each surface and the role played by hydrogen in these reaction processes.

After individual results are summarized, the results are compared and general mechanistic implications are presented.

On the stable square planar Ni(100) surface the dominant benzene formation process occurs at 270 K, above the hydrogen desorption temperature of 220 K. Increasing the availability of surface hydrogen by hydrogen preadsorption causes an increase of up to 37% in the benzene yield at 270 K for the saturated monolayer. Deuterium incorporation reveals that hydrogen primarily reacts to replace the bond broken in C–S bond scission. Increased hydrogen primarily increases the hydrogenation yield; however, HREELS data show that hydrogen also produces a reorientation of the bound thiolate species away from the surface. While very large preexposures of hydrogen reduce benzene yield though reorientation, no site blocking by hydrogen was observed in the uptake of benzenethiol on the Ni(100) surface.

On the close packed Ni(111) surface, the primary benzene formation process occurs at 260 K^{17,18} resulting from rapid hydrogenation of a phenyl group formed by C–S bond scission at 260 K. The desorption-limited hydrogen peak at 300 K removes free hydrogen from the surface. The addition of preadsorbed hydrogen causes a slight increase in the yield of benzene at 260 K but does not influence the temperature of the reaction as expected for a hydrogen addition step which is not rate limiting. Preadsorbed hydrogen also limits the amount of thiol which can adsorb on the surface, presumably through site blocking.

On the row and trough Ni(110) surface the reactions of benzenethiol are similar¹⁵ to the close packed Ni(111), but their rates increase. Benzene formation is observed near 220 K, just below the hydrogen desorption peak at 250 K. Preadsorbed hydrogen does not effect the yield of benzene but does cause a decrease in the reaction temperature by nearly 20 to 200 K. This decrease has been correlated with a reconstruction of the

Ni(110) surface by the preadsorbed hydrogen which would be expected to further facilitate bond activation. For example, increased activity of hydrogen has been observed for the hydrogenation of ethylene on the hydrogen reconstructed Ni(110) surface.²¹ Preadsorbed hydrogen does not block benzenethiol adsorption on the Ni(110) surface.

Comparison of C–S bond activation on the three low Miller index nickel surfaces indicates that hydrogen does not play a direct role in C–S bond activation under these conditions. The row and trough Ni(110) surface is most active for C–S bond activation as expected for an open surface which reconstructs at low temperature in the presence of sufficient hydrogen. C–S activation occurs 20–30° lower on this surface than on the Ni(100) surface. The close packed Ni(111) surface has an intermediate primary benzene desorption temperature, 10° below the benzene formation temperature on the Ni(100) surface. With the increased reactivity caused by hydrogen preadsorption on the Ni(110) surface attributed to reconstruction, the influence of hydrogen on the rate-limiting step for C–S bond activation appears to be limited to indirect effects related to hydrogen induced reconstruction of the Ni surfaces. However, hydrogen is clearly involved in the hydrogenation of adsorbed phenyl, which results in benzene formation. The influence of hydrogen availability is observed primarily in benzene yields.

The increased benzene yield observed with increasing hydrogen availability confirms that hydrogen is involved in benzene formation, as expected. Preadsorbed hydrogen causes a distinct (37%) increase in benzene yield on Ni(100), causes a very slight increase on Ni(111), and causes no increase in benzene yield on the Ni(110) surface. Hydrogen availability at the benzene formation temperature is clearly correlated with the influence of preadsorbed hydrogen on the benzene yield. On Ni(111) and Ni(110), hydrogen desorption occurs 30–40 K above the benzene peak so that benzene formation occurs in the presence of substantial free coadsorbed hydrogen. In contrast, on the Ni(100) surface, hydrogen desorption occurs 50 K below the benzene peak so that benzene formation occurs on a nearly hydrogen depleted surface. Thus additional hydrogen does not influence reaction on the Ni(111) and Ni(110) surfaces, where free hydrogen is available at reaction temperature. In the hydrogen deficient reaction of benzenethiol on Ni(100), coadsorbed hydrogen causes an increase in the availability of free hydrogen at the reaction temperature. This improves hydrogenation of the phenyl ring produced through C–S bond scission. In summary, hydrogenation/dehydrogenation selectivity is controlled by hydrogen availability, with increasing hydrogen availability promoting benzene formation.

Conclusions

C–S bond scission in benzenethiol on the Ni(100) surface leads primarily to benzene formation at 270 K. Preadsorption of hydrogen causes an increase in benzene yield of up to 37% and also causes an increase in the benzene formation temperature. Deuterium incorporation studies indicate that single hydrogen addition dominates, indicating that benzene formation occurs by hydrogen addition to an adsorbed phenyl group. The

rate-limiting C–S bond breaking step has been shown to involve direct reaction of phenylthiolate with the metal surface, followed by rapid hydrogenation to form desorbing benzene. Although hydrogen does not participate directly in C–S bond breaking, the importance of hydrogen availability in benzene formation was shown through a comparison of benzenethiol reactions on the three low Miller index surfaces of nickel. While sufficient surface hydrogen is present at reaction temperature on the Ni(111) and Ni(110) surfaces, hydrogen desorption prior to C–S bond activation on the Ni(100) surface clearly limits benzene formation.

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