Role of Hydrogen in Benzene Formation from Benzenethiol on the Ni(111) Surface

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The role of surface hydrogen in the desulfurization of benzenethiol to form benzene on the Ni(111) surface has been explored in hydrogen pressures ranging between UHV and up to 7×10^{-3} Torr. Hydrogen availability plays a significant role in the reaction of adsorbed benzenethiol, as demonstrated over a wide range of reaction conditions. Adsorbed hydrogen and phenylthiolate, formed from sulfur−hydrogen bond scission of the benzenethiol upon adsorption at 100 K, react with increasing temperature to produce the primary desorbing products benzene and hydrogen. The dominant benzene formation channel at high coverage occurs at 260 K, with a smaller benzene peak occurring at 290 K and a final benzene peak near 400 K. Increasing the availability of surface hydrogen does not significantly affect either the benzene yield or the benzene formation temperature for high benzenethiol coverage. The same reaction temperature is observed even for hydrogen pressures up to 7×10^{-3} Torr, as indicated by in situ temperature programmed fluorescence yield near edge spectroscopy (TP-FYNES) experiments. For low coverages of phenylthiolate on the clean Ni(111) surface, benzene formation decreases substantially and the higher temperature processes become more important. Hydrogen preadsorption in the low benzenethiol coverage case dramatically increases the amount of benzene formed at 260 K and decreases the high-temperature peak. Deuterium incorporation following reaction with coadsorbed deuterium clearly indicates three distinct levels of isotope incorporation for the benzene peaks at 260, 290, and 400 K. Incorporation of a single deuterium dominates for the peak at 260 K, indicating an adsorbed phenylthiolate intermediate dominates for this low-temperature process. Multiple incorporation dominates for the peak at 290 K, indicating a dehydrogenated intermediate of the "benzyne" type, which is also observed by vibrational spectroscopy. Benzene formed above 400 K includes even more extensive deuterium incorporation, suggesting an even more extensively dehydrogenated intermediate.

Introduction

Desulfurization is an industrially important reaction that has been studied by a variety of methods.[1−9] The mechanisms of hydrodesulfurization reactions have been studied by the adsorption and reaction of organic thiols on various single-crystal metal surfaces. The goal of this work is to characterize the role of surface hydrogen in the desulfurization of thiols, specifically benzenethiol, on the Ni(111) surface. The identification of surface intermediates is critical in understanding the complete reaction pathway.

Benzenethiol has been studied on the Mo(110),[10] Cu(110),[11] Rh(111),[12] Ni(110),[13] Ni(100),[14] and Ni(111)[15] surfaces using a range of UHV 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. The phenyl ring is typically found to be oriented either perpendicular or nearly perpendicular to the surface. On Mo-(110),[10] NEXAFS studies indicate a tilt of 23° away from the surface normal, while on Pt(111)[16] and Ag(111)[17] electrodes the ring was found to be perpendicular to the surface by HREELS. Phenylthiolate adsorbed in the 4-fold sites of

Ni(100)[14] has been found to bond with the C−S bond nearly normal to the surface, while on the Ni(110)[13] surface the phenyl group exhibits a tilt away from normal.

The desulfurization of benzenethiol has previously been studied on the Mo(110),[3] Ni(110),[13] and Ni(111)[15] surfaces. On Mo(110), thermal reaction leads to benzene desorption at 350 K, which was attributed to a slow hydrogenolysis of the C−S bond followed by fast desorption. At high temperatures, dehydrogenation forms surface benzyne, which is stable on Mo(110) to 680 K, where it decomposes to form hydrogen gas and surface carbon. The reactions of benzenethiol on Ni(110) also produce benzene from the surface thiolate, with desorption beginning at approximately 200 K. Additional benzene peaks are observed at high temperature. No spectroscopic evidence for benzyne on the Ni(110) surface was reported at any temperature.

Previous studies of benzenethiol adsorption and thermal reaction on the Ni(111) surface[15] have provided a valuable framework for the current work. HREELS indicates that the phenyl ring is tilted away from surface normal much like that for benzenethiol on Ni(110). Thermal reactions of low coverages of benzenethiol on Ni(111) lead to hydrogen evolution and surface-bound sulfur and carbon upon heating, as determined by TPD and AES. For higher initial benzenethiol

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coverages benzene is the primary reaction product formed by hydrogenation of phenylthiolate. Two primary pathways were discussed for the formation of benzene: a process limited by C−S bond scission at 263 K and a second, higher temperature, process at 400 K. HREELS studies have suggested a stable hydrocarbon intermediate above 300 K, while after heating to 800 K, complete decomposition occurs, leaving a complex $(\sqrt{39} \times \sqrt{39})$-S overlayer on the Ni surface.

An important facet of the benzene-producing reactions not previously explored, however, is the exact role of hydrogen. Preadsorption of hydrogen lowers the initial benzene formation temperature on the Ni(110) surface.[13] Methanethiol also undergoes hydrogen-induced bond activation on the Pt(111) surface.[18] The purpose of this study is to explore the role of hydrogen on the reaction of benzenethiol on the Ni(111) surface. In addition to the UHV techniques of TPD, AES, LEED, and HREELS, experiments utilizing temperature-programmed fluorescence yield near edge spectroscopy (TP-FYNES) were performed, allowing hydrogen pressures up to 7×10^{-3} Torr to be examined. Careful control of reaction conditions allows for the determination of the influence of hydrogen on the benzene-forming reaction and the development of a detailed reaction scheme for benzenethiol adsorption and reaction on Ni(111).

Experimental Section

These experiments were performed in one of two stainless steel UHV chambers, each of which has been described in detail elsewhere.[15,19] TP-FYNES experiments were performed at the U1A beamline at the National Synchrotron Light Source. The chamber consists of a high-pressure reaction cell mounted on top of a standard chamber which included equipment for TPD, Auger, and ion sputtering. The clean crystal was dosed with benzenethiol and then raised into the high-pressure cell, which could be isolated from the lower chamber. Experiments were run either at vacuum or at high pressures of hydrogen, with the maximum pressure being limited to 7×10^{-3} Torr by the seal on the window to the synchrotron ring. The FYNES detector has been described in detail previously.[19] TP-FYNES spectra were taken at 300 eV, in the carbon continuum. This allows for the determination of total carbon content as a function of time and temperature. Spectral intensity was measured before hydrogen addition, throughout thermal reaction, and after hydrogen removal to account for any change in the background spectra. Total carbon coverage following reaction was referenced to the AES.

TPD and HREELS experiments were performed in a separate UHV chamber at ORNL with a base pressure of 1×10^{-10} Torr. This chamber was also equipped with AES, LEED, and a sputter gun. The Ni(111) 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. A type E thermocouple was 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.[13] 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. Rapid heating (20 K/s) was used to reach the desired reaction temperature in the isothermal desorption experiments. HREELS data was obtained using a LK2000-DAC spectrometer with an experimental resolution of 4−6 meV.
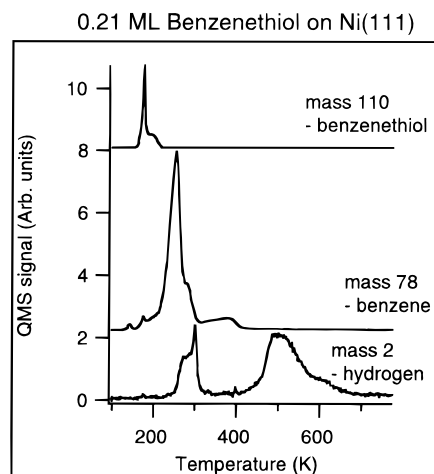

Figure 1. Primary reaction products for saturated benzenethiol overlayer on the Ni(111) surface. Excluding physisorbed benzenethiol, the only products found to desorb are benzene and hydrogen.

In all experiments, benzenethiol was purified by several freeze−pump−thaw cycles. At the ORNL facilities, the crystal was positioned within 1 mm of a directional doser and benzenethiol was dosed through a 19 μm laser-drilled aperture. The pressure behind the aperture was controlled by placing the benzenethiol in an ice water bath (0 °C). Dosing at NSLS involved the use of a directional doser as above, but used a leak valve to expose the crystal to a given pressure for a set period of time. Hydrogen, deuterium, and sputter gases were dosed by backfilling the chamber through a leak valve and were used without further purification. The purity of these gases was confirmed by regular mass spectroscopy checks.

The uptake of benzenethiol was monitored by AES. No sulfur-containing species desorb from the surface below saturation coverages, so that the S(152 eV) Auger peak following complete thermal reaction is proportional to the initial coverage of adsorbed benzenethiol. The previous study determined the saturation coverage of benzenethiol on Ni(111) to be 0.21 ML, where 1 ML represents one sulfur atom for every nickel atom, by comparison to a fully sulfur saturated surface produced by H_2S adsorption,[15] which produces a sulfur coverage of 0.40 ML.

Results and Discussion

The desorption products for 0.21 ML of benzenethiol are benzene and hydrogen and are shown in Figure 1. At this coverage, benzene desorbs in three features between 250 and 450 K as seen previously.[15] The low-temperature desorption peaks at 260 K, with a shoulder occurring at 290 K. A final small desorption of benzene is observed between 350 and 400 K. A small benzene peak at 150 K is attributed to slight benzene contamination, which was found not to influence surface reaction. The desorption of hydrogen occurs at 300 K from the recombination of free surface hydrogen from initial thiol decomposition[15] and at 510 K, which can be attributed to dehydrogenation of surface hydrocarbons. An additional hydrogen feature of note is the sharp spike just above 300 K, correlating with the 290 K benzene desorption, which is attributed to the partial dehydrogenation of surface-bound aromatic rings. The only other desorbing species observed was molecular benzenethiol (at $m/e = 110$) from a slight multilayer which produced fragment peaks in both the benzene and hydrogen desorption profiles at 200 K.

The influence of hydrogen coverage on the kinetics of benzenethiol desulfurization is of great interest. Figure 2 shows the benzene desorption for saturation coverages of benzenethiol
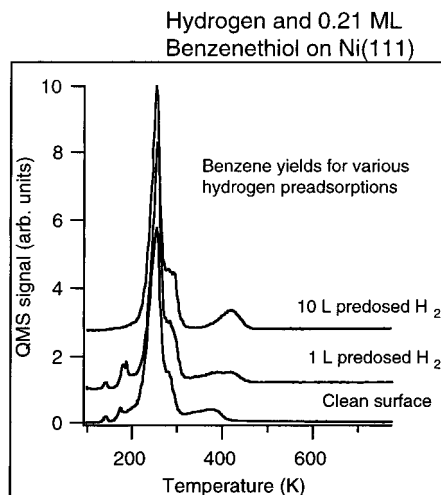
Hydrogen and 0.21 ML
Benzenethiol on Ni(111)

Figure 2. Saturated benzenethiol on the clean and hydrogen-pretreated Ni(111) surface. Hydrogen is shown to decrease the amount of high-temperature benzene formed and causes a shift in the high-temperature peak. The low-temperature benzene formation is essentially unaffected by preadsorbed hydrogen.

with selected amounts of hydrogen preadsorbed on the Ni(111) surface. AES data show a decrease in thiol uptake of approximately 20% on the hydrogen presaturated surface. However, there is no change in the dominant benzene desorption temperature for this range of hydrogen and benzenethiol exposures. Interestingly, the high-temperature benzene desorption increases in temperature as the exposure to hydrogen increases. This is interpreted as an increase in the stability of the intermediate fragments on the surface associated with a lower hydrocarbon coverage at high temperature. The reaction temperature is similar to that of low coverages of benzenethiol, discussed below. Additionally, the 260 K benzene yield increases slightly relative to total adsorbed thiol in the hydrogen-pretreated case. Peaks occurring near 200 K are attributed to fragmentation of benzenethiol during multilayer desorption.

UHV studies have indicated that hydrogen does not change reaction temperature for up to 10 langmuirs of preadsorbed hydrogen at high benzenethiol exposures. Utilizing TP-FYNES, we have studied adsorbed benzenethiol hydrogenolysis in up to 7×10^{-3} Torr of hydrogen. Figure 3 shows the TP-FYNES spectra acquired for saturation coverage of benzenethiol at a heating rate of 0.5 K/s in vacuum and in hydrogen gas. Lines were obtained by extensive smoothing of the data and are meant to guide the eye. The final carbon remaining on the surface in the presence of hydrogen is significantly lower than in the absence of hydrogen. The difference in the shape of the curve above 300 K suggests that high-temperature benzene is no longer produced, which indicates hydrogen availability may play a role in benzenethiol reaction at lower temperatures. This is supported by AES data which indicate that there is no surface carbon left on the surface following reaction in hydrogen. However, the onset temperature for C−S bond scission is unchanged for all hydrogen pressures examined. A change in the activation energy of C−S bond cleavage should produce a curve with a different initial slope, which is not observed.

It is interesting that hydrogen, which has exhibited a significant effect on the C−S bond activation temperature for benzenethiol on Ni(110),[13] does not affect C−S bond activation on Ni(111). Preliminary data also indicate that hydrogen does not influence reaction temperature for benzenethiol reaction on the Ni(100)[20] surface either. The increased activity of Ni(110) relative to the other nickel surfaces may be attributed to the hydrogen-induced reconstruction of the Ni(110) surface to a
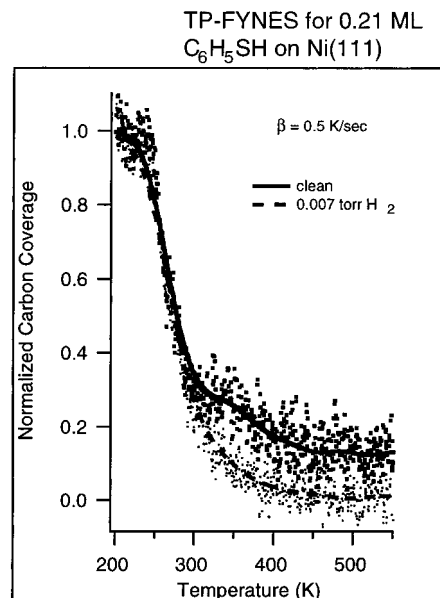
TP-FYNES for 0.21 ML
C_6H_5SH on Ni(111)

Figure 3. TP-FYNES spectra of benzenethiol on Ni(111) in vacuum and at 7×10^{-3} Torr H_2. These experiments provide a measure of total surface carbon coverage. Hydrogen reduces the amount of carbon present at high temperature, likely driving the high-temperature benzene formation completely away. No effect on C−S bond scission temperature is observed at this pressure of hydrogen. (the lines were obtained by extensive smoothing of the data and are meant to guide the eye.)

(1×2)-reconstructed phase, which enhances hydrogenation.[21] This reconstruction is not induced by hydrogen for either Ni(111) or Ni(100).

The adsorption of a subsaturation coverage of benzenethiol can be used to further clarify the role of hydrogen and to characterize the steps in the formation of benzene. The desorption profile for 0.10 ML of benzenethiol on Ni(111) is shown in the right panel of Figure 4. Several important differences are observed between the benzene formation profiles of the 0.21 ML (Figure 1) and 0.10 ML coverages. Most noticeable is that the 260 K benzene peak is no longer the most prominent reaction pathway for low coverages. The high-temperature benzene desorption is now moderately larger than the low-temperature benzene peaks. The high-temperature peak is also shifted to a higher temperature compared to saturation coverages of benzenethiol. The benzene desorption feature at 290 K can be clearly seen in the low-coverage case, showing this to be a process separate from the 270 K benzene desorption. A similar shoulder for methanethiol on the Ni(111)[19] surface was attributed to a different adsorption site for the thiolates. However, in the case of benzenethiol, the temperature dependence of the XPS peaks shows no new surface species.[15]

The sole source of hydrogen in the previously described experiment was that formed from sulfur−hydrogen bond scission upon adsorption. Two likely causes for the differences between the 0.21 and 0.10 ML experiments are the availability of one or both of the adsorbed reactants and a change in the bonding of the surface reactants. The availability of hydrogen was probed by the preadsorption of hydrogen on the Ni(111) surface. The preadsorption of molecular hydrogen causes significant changes in the reaction selectivity for a 0.10 ML coverage of benzenethiol. The left panel of Figure 4 shows a benzene formation peak that is almost identical in temperature and shape to that for the 0.21 ML coverage. The similarity between benzene desorption profiles for the low-coverage, hydrogen-pretreated case and the untreated, fully saturated
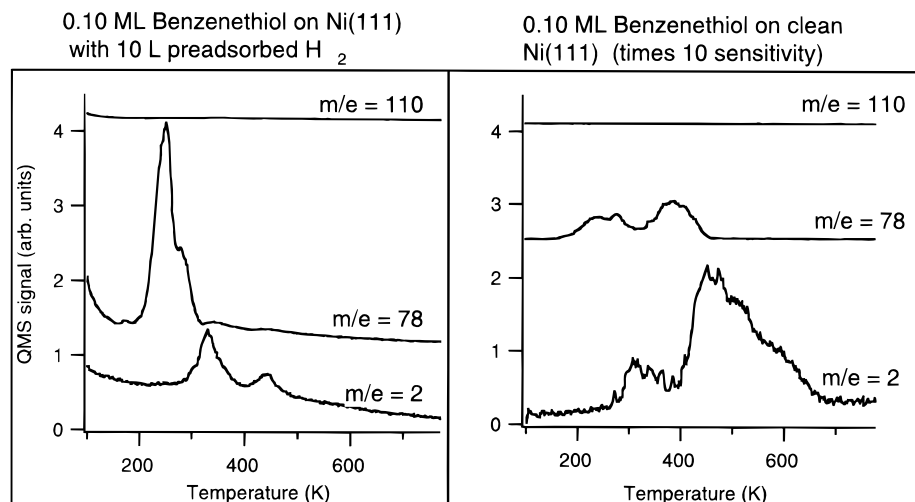
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Figure 4. 0.10 ML coverage of benzenethiol on clean (right) and hydrogen-predosed Ni(111) (left). High-temperature benzene formation dominates for the clean surface case, while hydrogen influences reaction selectivity toward low-temperature benzene formation. The sensitivity of the clean surface spectrum is 10 times that of the hydrogen-pretreated experiment.

experiment indicates that hydrogen availability is important to the low-temperature benzene-forming reaction.

The possibility of a change in surface bonding of the thiolate was also considered as an explanation of the difference between the low and high benzenethiol coverage experiments. HREELS data indicate that for 0.10 ML coverage of benzenethiol the orientation of the ring is similar to the saturated benzenethiol layer (specifically, tilted from surface normal). The dipole selection rule was used to determine orientation from dipole active modes of the adsorbate which were determined experimentally. Specifically, the energy loss occurring at 730 cm^{-1} attributed to the C−H out of plane bend[15] of the phenyl ring was found to be dipole active, and the strongest intensity should occur as the ring became more parallel to the surface. Comparison of the 0.10 ML benzenethiol spectrum with the HREELS spectrum of the same coverage of benzenethiol on a 10 langmuir H$_2$-pretreated surface shows that there is no significant change in the orientation of the phenyl ring prior to reaction. This limits the probability that the change in reactivity is caused by a reorientation of the surface thiolate. This HREELS data and the preadsorption of hydrogen at low thiolate coverage together clearly indicate that hydrogen plays the major role in the reaction of adsorbed benzenethiol to form benzene.

Vibrational spectroscopy was used to identify species on the surface at several stages of reaction. The HREELS data for several annealing sets is shown in Figure 5. At 90 K, the multilayer is clearly indicated by the presence of the (τ S−H) stretch at 200 cm^{-1} and the S−H stretch at 2550 cm^{-1}. Also notable is the loss at 470 cm^{-1}, which is attributed to the Ni−S−C stretch. Annealing to 190 K removes physisorbed benzenethiol and shows the surface species to be adsorbed phenylthiolate. Sulfur−hydrogen bond scission is confirmed by the absence of the S−H stretching modes at 200 and 2250 cm^{-1}. Additional features used to identify the phenylthiolate intermediate are the out-of-plane C−H bends at 730 and 1166 cm^{-1}, C−C stretches at 1454 and 3055 cm^{-1}, and a combination of the in-plane C−H bend and a C−C stretch at 1004 cm^{-1}. After an anneal at 240 K for 60 s to remove the initial benzene producing species, HREELS data indicate that the remaining surface species retains its aromatic ring structure and is oriented nearly perpendicular to the surface, as seen in the intensity loss at 730 cm^{-1}, determined earlier to be dipole active, relative to the other transitions. Another important feature of the 240 K spectrum is the shift in the position of the former Ni−S−C transition to 435 cm^{-1}. This new value is indicative of a Ni−S
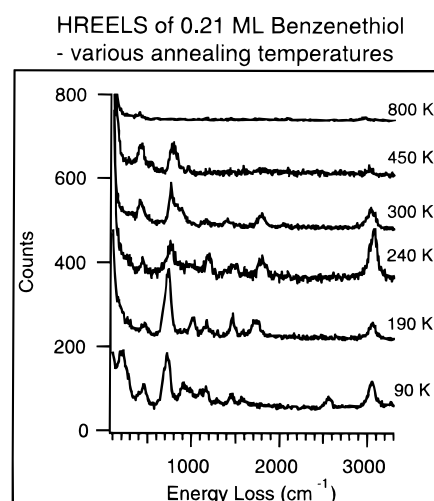

Figure 5. HREELS spectra of benzenethiol on Ni(111) at various temperatures. For each spectrum, the sample was annealed to the temperature shown for 60 s (except the 240 K anneal, which was held for 240 s to ensure complete removal of species contributing to the 260 K benzene desorption) and the spectrum recorded at 90 K. The small peak near 1750 cm^{-1} in some of the spectra is due to the presence of impurity CO.

stretch and shows that the C−S bond has indeed been broken by this temperature and that the remaining hydrocarbon is free of sulfur. This is in agreement with XPS data from the previous study,[15] which showed a marked increased in the atomic sulfur peak at 161.2 eV above these temperatures. The orientation of this hydrocarbon species is unchanged in the presence of coadsorbed hydrogen. In our previous study, we did not characterize this species in detail. The HREELS data after annealing to 240 K exhibit a loss of intensity of the β(C−H) + ν(C−C) mode at 1000 cm^{-1}, with an accompanying increase in the intensity of the peak at 1100 cm^{-1}. This is very similar to the HREELS spectrum of surface benzyne observed on Mo(110)[10] and Rh(111).[12] Above 300 K, the HREELS spectra indicate a different dehydrogenated cyclic species adsorbed largely parallel to the surface, identified by the strong intensity of the 730 cm^{-1} loss relative to other features in the HREELS spectrum. Annealing to 450 K, above the final benzene-producing temperature, yields an HREELS spectrum attributed to nondesorbing hydrocarbon fragments which finally decompose to leave only the Ni−S vibration at 800 K. The appearance of a peak near 1750 cm^{-1} in the data obtained following low-
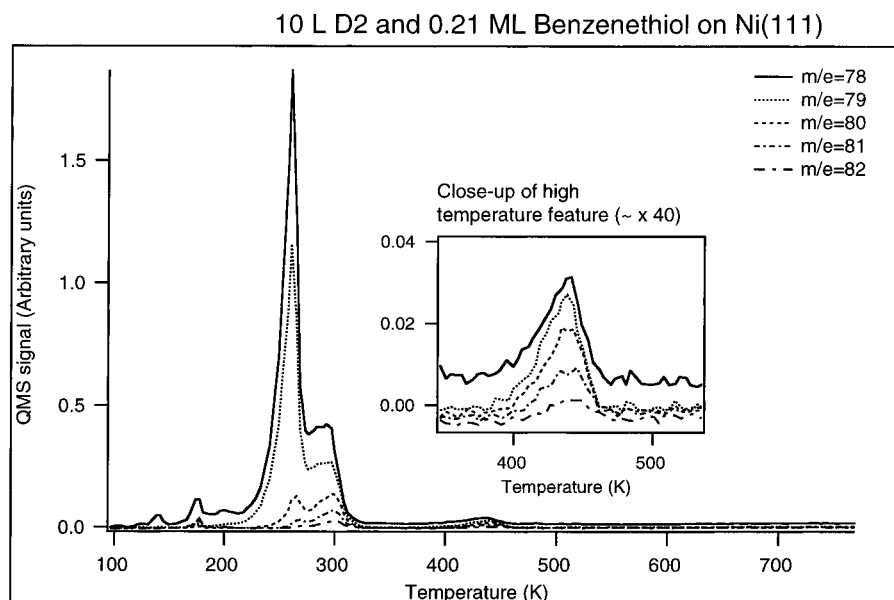
Figure 6. Incorporation of deuterium into the benzene product from coadsorbed D_2 (10 langmuirs) and benzenethiol on Ni(111). Three distinct isotope incorporation patterns are observed at 260, 290, and 390 K (shown in the inset), indicating three different hydrocarbon species.

Reaction pathway diagram for ddsorbed benzenethiol
(0.21 and 0.10 ML coverages) in vacuum and in the
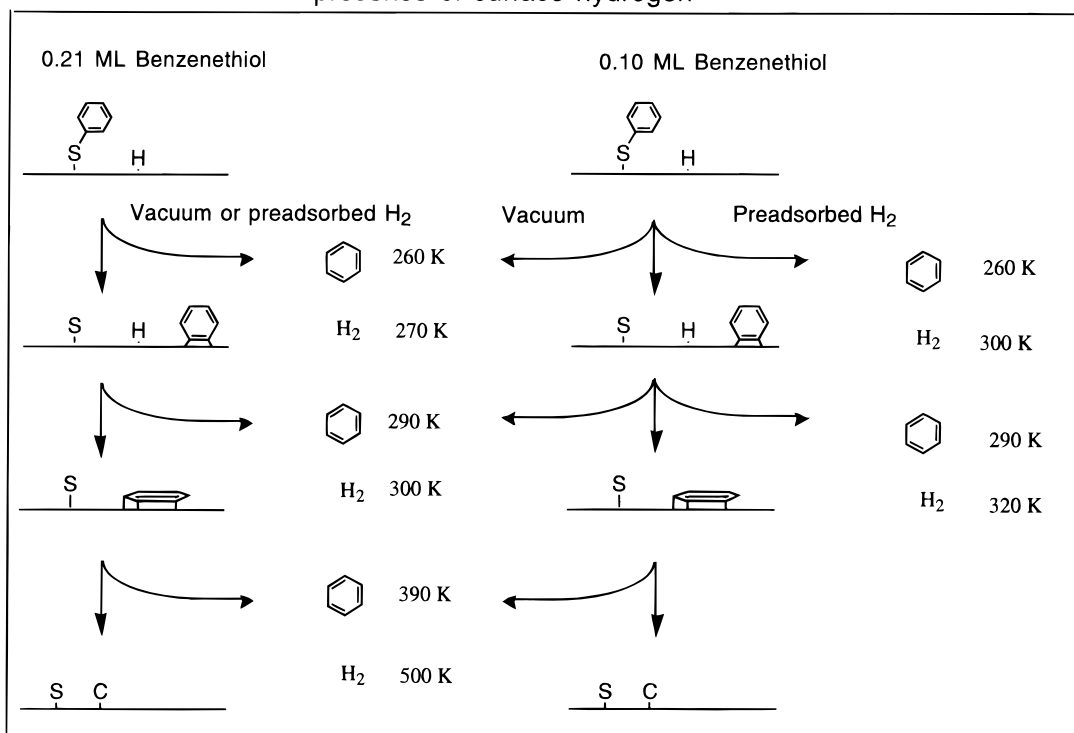presence of surface hydrogen

Figure 7. Schematic of the reaction mechanism for benzenethiol reaction on the Ni(111) surface at high and low coverages, including the effect of hydrogen.

temperature (<450 K) anneals is attributed to trace amounts of CO on the surface.[15]

Deuterium incorporation studies were performed to facilitate the identification of surface species and the role of hydrogen in their reactivity. TPD spectra for deuterium incorporation are shown in Figure 6. Monodeuterated benzene ($m/e = 79$) is the primary deuterated product, while the C_6H_6 benzene is dominant. Deuterium incorporation up to benzene-d_4 was detected in these experiments. The incorporation of deuterium into the smaller 290 K benzene peak is more extensive than for the low-temperature peak. For species with higher deuterium incorpora-

tion, the 290 K peak is actually greater than the low-temperature peak. This indicates a greater interaction of the ring with the surface prior to desorption at 290 K. This correlates well with the proposed benzyne group suggested by HREELS. Extensive incorporation of deuterium into the desorption peak above 400 K is also indicative of a dehydrogenated cyclic surface species.

The general reaction scheme for saturated monolayers of benzenethiol on Ni(111) is illustrated in Figure 7. Benzenethiol monolayers dehydrogenate to form phenylthiolate and surface hydrogen at 100 K, with physisorbed benzenethiol desorption

occurring at 190 K. The saturation coverage of 0.21 ML produces a layer of phenylthiolate with an orientation tilted away from the surface normal. Initial formation of benzene occurs simultaneously with C−S bond scission. Additional external hydrogen did not influence the temperature of this reaction, implying hydrogen does not change the activation energy for C−S bond scission. Hydrogen does, however, increase the extent of the low-temperature reaction, shown most clearly in submonolayer coverages of benzenethiol. The next reaction feature is the small benzene formation peak found at 290 K. HREELS data and deuterium incorporation suggest that the intermediate for this reaction channel is most likely an adsorbed benzyne-like species. Further heating eventually produces additional benzene desorption near 400 K. This reaction intermediate is identified as a highly dehydrogenated cyclic intermediate oriented largely parallel to the surface. This product can be radically altered by the presence of hydrogen, largely due to the removal of aromatic hydrocarbon by the low-temperature reaction as described above and the stabilization of the surface phenyl group. Finally, the remaining hydrocarbon fragments decompose, leaving only surface sulfur. AES indicates a slight trace of carbon remains on the surface, but is not readily quantifiable due to the propensity of nickel toward absorbing carbon into the bulk.

Conclusions

The factors influencing the formation of benzene from benzenethiol adsorbed on Ni(111) have been characterized by this study. Adsorbed hydrogen and phenylthiolate, formed from sulfur−hydrogen bond scission of the benzenethiol upon adsorption at 100 K, react with increasing temperature to produce the primary desorbing products benzene and hydrogen. C−S bond scission occurs below 260 K, producing a phenyl group which reacts in a fast step with available hydrogen to produce the initial benzene desorption, which peaks at 260 K. The low-temperature benzene formation reaction was demonstrated to depend on the availability of surface hydrogen, although the energetics of the reaction were not affected by additional hydrogen up to a pressure of 7×10^{-3} Torr. While the presence of hydrogen produced little effect at high coverages of benzenethiol, the effect of hydrogen preadsorption was dramatic at the intermediate coverage of 0.10 langmuir benzenethiol. A smaller benzene peak occurs at 290 K from the hydrogenation of a dehydrogenated aromatic, benzyne-like species oriented largely perpendicular to the surface plane. This is demonstrated clearly by the greater extent of deuterium incorporation from coadsorbed deuterium into the benzene desorbing at this temperature and the sharp hydrogen desorption immediately following the benzene peak in temperature and confirmed by HREELS. The third and final benzene peak is observed near 400 K and is attributed to the hydrogenation of an even more extensively dehydrogenated cyclic intermediate. At 800 K, complete decomposition of any remaining organic compounds leaves sulfur and traces of carbon on the surface, yielding a $(\sqrt{39} \times \sqrt{39})$ LEED pattern.

Understanding the role of hydrogen is of great importance in the study of desulfurization reactions. While some previous studies have shown hydrogen to lower the activation energy of

C−S bond cleavage, the temperature of bond scission for benzenethiol on the Ni(111) surface has been found to be independent of hydrogen, even up to high pressures. While the temperature of C−S bond scission was not affected by surface hydrogen, the reaction selectivity was critically dependent on the presence of excess hydrogen at low phenylthiolate coverages. The importance of hydrogen in reaction selectivity has also recently been demonstrated in the reactions of thiophenic compounds on the Ni(111) surface[22] and in the cross reaction of methanethiol and benzenethiol to produce toluene on both the Ni(111) and Ni(100) surfaces.[23,24]

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