Toluene Formation from Coadsorbed Methanethiol and Benzenethiol on the Ni(111) Surface

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We report our observation of interspecies carbon−carbon bond formation during the reaction of coadsorbed methanethiol and benzenethiol on the Ni(111) surface. Toluene formation has been detected between 250 and 320 K in addition to methane and benzene, the hydrogenolysis products. Increased concentrations of benzenethiolate and methanethiolate, the surface intermediates, increase the amount of toluene formed. As observed previously during methanethiol decomposition, a small amount of ethane was produced[1] in addition to the cross-coupling product; however, no biphenyl was observed by temperature-programmed desorption. On adsorption at 100 K, dissociation of the sulfur−hydrogen bond in both thiols results in the formation of a stoichiometric amount of the adsorbed thiolate and adsorbed hydrogen. Addition of external hydrogen decreases the amount of toluene produced up to 25% from the untreated surface yield, despite the presence of hydrogen from thiol dissociation. Oxygen pretreatment of the Ni surface results in increased toluene production for a wide range of coadsorbed thiolate coverages. Water formation below the toluene formation temperature decreases surface hydrogen, causing the toluene yield to increase substantially compared to methane and benzene yield. Toluene increases up to a factor of 20 were observed for high coadsorbed coverages. Together these results clearly indicate that competition between hydrogen addition and alkylation controls toluene formation.

Alkylation is typically performed in industry by the reaction of alkanes and olefins in HF or H_2SO_4 reactors.[2] Benzene alkylation usually involves a Friedel−Crafts reaction of the phenyl ring with alkyl halides over an $AlCl_3$ catalyst.[3,4] Studies have also examined carbon−carbon bond formation with solid acids,[5,6] zeolites,[7] molten salts,[8] and transition metal complexes.[9,10] Carbon bond formation reactions have been studied on several metal surfaces, including organohalide reactions on Cu,[11−13] Au,[14,15] and Pd[16] and methyl radical reactions on Pt.[17]

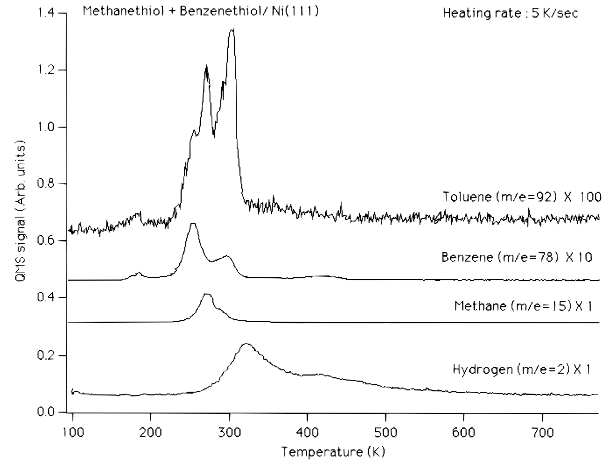

Figure 1. Thermal desorption spectra taken after methanethiol exposure sufficient to produce a saturation coverage (0.25 ML) followed by an equivalent exposure of benzenethiol on the Ni(111) surface.

Adsorbed thiols, such as benzenethiol or methanethiol, have been characterized mainly for understanding carbon−sulfur bond activation,[1,18−22] lubrication,[23] and the properties of self-assembled monolayers.[24] On most metal surfaces, the sulfur−hydrogen bond dissociates on adsorption, leaving surface hydrogen and the thiolate bound to the surface. Thermal reaction of the thiolate typically leads to hydrogenolysis to form the corresponding hydrocarbon or nonselective surface decomposition. Carbon−carbon bond formation has not previously been observed for two coadsorbed organothiols.

The equipment used in this experiment has been described in detail previously.[19] Products are studied by temperature-programmed reaction, following adsorption on a clean or predosed Ni surface. The crystal was heated at 5 K/s and temperature−intensity profiles were collected for several masses. Adsorbed thiol coverages were determined by measuring final sulfur coverages with Auger electron spectroscopy after annealing. No sulfur-containing species except the physisorbed thiols desorb from the Ni surface in the temperature range under observation, so final sulfur coverages accurately reflect initial total thiolate coverages. The thiols were purified by several freeze−pump−thaw cycles and applied through separate directional dosers, with the crystal positioned within 1 mm of each doser. H_2 and O_2 were dosed by back-filling the chamber to a specified pressure for a set period of time.

The coadsorption of a selected range of methanethiol and benzenethiol exposures was examined. In addition to the amounts of thiols dosed, the effect of dosing order was investigated. Extensive data for each thiol separately have been reported previously for the Ni(111) surface.[1,19] The primary products of the reactions of the individual thiols are hydrocarbons formed from hydrogenolysis of the sulfur−carbon bond. Experiments have shown that adsorbed alone on a clean surface, methanethiol produces methane at 273 K[1] and benzenethiol forms a series of benzene desorption peaks above 265 K.[19] Figure 1 shows the reaction products observed following an

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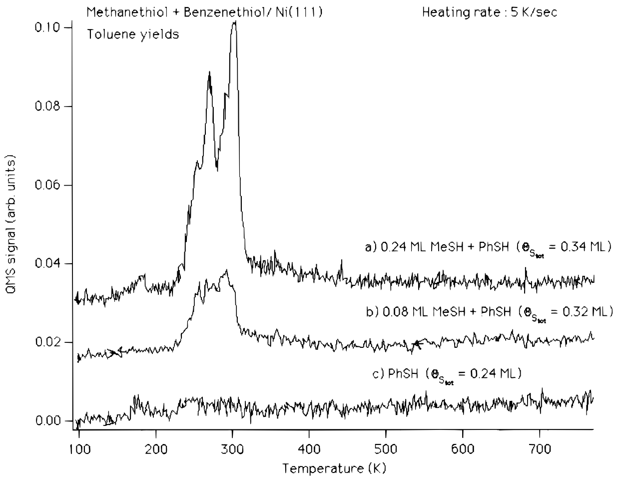

Figure 2. Thermal desorption spectra of toluene from (a) saturation exposure of methanethiol (0.25 ML) followed by equivalent exposure to benzenethiol, (b) low exposure (0.08 ML) of methanethiol followed by saturation exposure of benzenethiol, and (c) benzenethiol adsorbed in the absence of predosed methanethiol. Final sulfur coverages resulting from the coadsorption experiments are indicated.

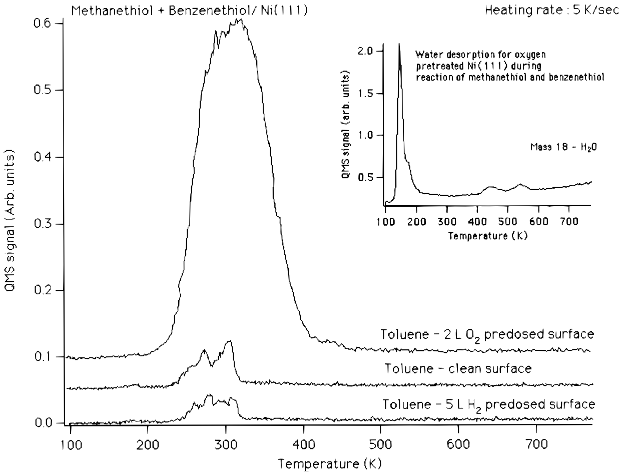

Figure 3. Thermal desorption spectra of toluene desorption from the Ni(111) surface predosed with oxygen, hydrogen, and a clean surface followed by approximately half-saturation coverages each of methanethiol and benzenethiol. Inset shows water desorption prior to toluene formation for the oxygen-predosed case.

exposure sufficient to give 0.25 ML (approximately saturation) of methanethiol followed by an equivalent exposure of benzenethiol. Toluene is formed and desorption begins at 250 K and is complete by approximately 320 K. A smaller toluene formation peak is centered at 380 K. Submonolayer coverages of toluene have been observed to undergo complete decomposition on the Ni(111) surface.[25] Low-temperature (100 K) adsorption of toluene performed for this study also leads to complete decomposition for submonolayer coverages. *For coadsorbed thiols*, hydrogen, methane, and benzene are the other major products which desorb from the surface, while trace amounts of ethane have been detected, similar to previous methanethiol decomposition experiments.[1] The methane and benzene desorption peaks are very similar to the peaks formed during decomposition of each thiol individually on a clean Ni(111) surface. The correlation between toluene desorption and thiolate hydrogenolysis indicates that toluene formation is limited by carbon−sulfur bond activation. A crude estimate of the relative yields can be found by correcting the observed peak intensities for the ionization efficiencies and mass spectrometer transmission function for each molecule. This information can also be related to absolute coverage through comparison to monolayers of each thiol alone on the Ni(111) surface. Maximum yields of toluene from the initially clean surface were found to be slightly less than 1% of the total products desorbing from the surface, which accounts for approximately 0.003 ML. Figure 2 indicates that the amount of toluene formed increases with increasing methanethiol predosed exposure and a constant benzenethiol exposure equivalent to saturation of a clean surface. A similar pattern was observed when the order of adsorption was reversed. No additional carbon−carbon bond formation products were detected from reaction of coadsorbed methanethiol and benzenethiol.

The selectivity of the coupling reaction relative to hydrogenolysis has been probed by increasing and decreasing the availability of surface hydrogen at coupling temperatures as illustrated in Figure 3. Addition of external hydrogen to increase the availability of surface hydrogen should decrease the amount of coupling observed if competition is a primary controlling factor. Toluene formation decreases up to 25% have been observed. Substantial amounts of hydrogen are available on the surface from low-temperature thiol decomposition prior to external hydrogen addition. The small decrease in toluene produced is consistent with a small increase in availability. The decrease is largest for intermediate and small coverages of coadsorbed methanethiol followed by benzenethiol. The decrease was measured relative to the total amount of thiol adsorbed to compensate for any variations in initial thiol coverage caused by hydrogen predosing. Avenues for further exploring the effect of surface hydrogen require the elimination of hydrogen formed from sulfur−hydrogen bond dissociation. On Pt[26] and Ni[27,28] surfaces, water is formed from the reaction of H_2S with preadsorbed oxygen. Addition of 2 L (1 L = 1 × 10^{-6} Torr s) of preadsorbed oxygen, annealed to 600 K, causes low-temperature water formation at 190 K which decreases the amount of hydrogen available at coupling temperature (see inset, Figure 3). Thus, oxygen addition is expected to increase the formation of toluene if competition with hydrogenolysis is a primary controlling factor. Increases in toluene formation up to a factor of 20 have been observed with preadsorbed oxygen for a wide range of initial coadsorbed coverages and for two different coverages of preadsorbed oxygen. Toluene yield accounts for approximately 22% of the total desorbing products, equivalent to 0.06 mL, demonstrating that the reaction selectivity is indeed controlled by competition with hydrogenolysis.

We have established both that carbon−carbon bond formation occurs from coadsorbed methanethiol and benzenethiol on the Ni(111) surface and that the selectivity is enhanced when the competing hydrogenolysis mechanism is hindered. This provides significant insight into a novel and catalytically important type of surface reaction.

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