

Investigation of the Adsorption and Reactions of Thiophene on Sulfided Cu, Mo, and Rh Catalysts[†]

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The surface chemistry of thiophene (C_4H_4S) on sulfided Cu/Al_2O_3 , Mo/Al_2O_3 , and Rh/Al_2O_3 catalysts has been investigated under well-defined conditions using infrared (IR) spectroscopy and temperature programmed desorption (TPD). The results of these experiments have been found to correlate nicely with CO chemisorption measurements of site densities and thiophene hydrodesulfurization (HDS) activities measured in a flow reactor system. In agreement with the literature, the catalysts were found to have dramatically different thiophene HDS activities increasing in the following order: sulfided $Cu < sulfided Mo < sulfided Rh$. The trend of HDS activities is mirrored in similar trends for the site densities and turnover frequencies for the sulfide catalysts. IR spectra of adsorbed thiophene on the sulfided Cu, Mo, and Rh catalysts at low temperatures show that the amount of thiophene adsorbed on the metal sites of the sulfide catalysts correlates with the CO chemisorption estimates of site densities. Thiophene reactivity on the catalysts differs significantly, with reaction in thiophene/ H_2 mixtures observed on the sulfided Mo and Rh catalysts annealed at 300 and 500 K, respectively, and not at all on a sulfided Cu catalyst annealed up to 700 K. Strongly adsorbed species produced on the sulfided Cu, Mo, and Rh catalysts during the annealing sequence were subjected to TPD experiments that yielded C_4 hydrocarbons and H_2S , with the predominant C_4 product being butenes. IR and TPD measurements of 1,3-butadiene and 1-butene on sulfided Rh/Al_2O_3 catalysts, both in the pure gas and in gas/ H_2 mixtures, provide evidence for the tentative assignment of strongly adsorbed species produced by cleavage of C–S bonds in thiophene to be a σ -bonded allyl species with C_4H_7 stoichiometry.

Introduction

In the 1980s, at least three studies appeared in the catalysis literature which showed that the hydrodesulfurization (HDS) activities of second and third row transition metal sulfide catalysts exhibit a volcanic-type dependence upon the position of the transition metal in the periodic table.^{1–3} This trend was observed to hold for unsupported and carbon-supported transition metal sulfides and for two different organosulfur compounds: thiophene and dibenzothiophene. The authors of these studies proposed explanations for the volcano-type dependence of HDS activity in terms of the metal–sulfur bond strength,¹ the metallic character of the sulfides,² and the structures of the sulfides.³ Theoretical investigations have identified electronic factors, including the number of electrons in the highest occupied molecular orbital (HOMO),⁴ the cohesive energy per metal–sulfur bond,^{5,6} and the metal–sulfur bond energies^{7–9} for the transition metal sulfides, as possible explanations for this behavior. The cohesive energy per metal–sulfur bond and the metal–sulfur bond energies are calculated in different ways, and the authors of these studies interpret their results differently. Toulhoat and co-workers^{5,6} conclude that transition metal sulfides with intermediate metal–sulfur bond strengths should have the highest HDS activities, while Nørskov and co-workers^{7–9} conclude that transition metal sulfides with the lowest metal–sulfur bond strengths should have the highest HDS activities.

In this work, we have undertaken a study of the adsorption and reactions of thiophene on alumina-supported transition metal

sulfides possessing dramatically different HDS activities. Infrared (IR) spectroscopy and temperature programmed desorption (TPD) were used to investigate the surface chemistry of thiophene on sulfided Cu/Al_2O_3 , Mo/Al_2O_3 , and Rh/Al_2O_3 catalysts over wide ranges of temperature (140–700 K) and pressure (10^{-9} –300 Torr). The results of these experiments correlate well with thiophene HDS activities measured for these same catalysts in an atmospheric pressure flow reactor.

Experimental Section

Sample Preparation. The sulfided transition metal catalysts were supported on $\gamma-Al_2O_3$ (Engelhard AL-3945) that had a BET surface area of 255 m^2/g and a pore volume of 0.60 mL/g. The alumina support (1/12-in. extrusions) was ground to a fine powder prior to use. Samples of the alumina support were impregnated with aqueous solutions of ammonium heptamolybdate (J. T. Baker), rhodium(III) trichloride (Johnson-Matthey), and copper(II) nitrate (J. T. Baker) to give their respective catalyst precursors, each with similar metal loadings. Following impregnation, the catalyst precursors were dried for 24 h at 393 K and were then calcined for 3 h at 773 K in air, yielding oxidic catalysts with the following loadings: Cu/Al_2O_3 (8.2 wt % CuO), Mo/Al_2O_3 (14.3 wt % MoO_3), and Rh/Al_2O_3 (12.9 wt % Rh_2O_3).

BET and Pulsed Chemisorption Measurements. BET surface area and CO pulsed chemisorption measurements were carried out using a Micromeritics Pulse Chemisorb 2700 apparatus. For both types of measurements, catalyst samples (~0.10 g) were placed in a quartz U-tube (15 mm o.d.), dried in air at 393 K, and then degassed in flowing He (45 sccm) for 2 h at 673 K. Following degassing, the catalyst samples were

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sulfided for 2 h in a 60 sccm flow of a 3% H₂S/H₂ mixture at 623 K. After sulfidation, the catalyst samples were reduced in a 60 sccm flow of H₂ at 573 K (Cu/Al₂O₃ and Rh/Al₂O₃) or 623 K (Mo/Al₂O₃) for 1 h. The catalysts were submitted to a final degassing in flowing He (60 sccm) at 623 K (Cu/Al₂O₃ and Rh/Al₂O₃) or 673 K (Mo/Al₂O₃) for 1 h prior to cooling to room temperature. The He and H₂ utilized in the chemisorption system were passed through 5 Å molecular sieve and O₂ purification traps prior to use.

Single-point BET surface area measurements were carried out using a 28.6% N₂/He mixture (Airco). The instrument was calibrated prior to the BET measurements using pure N₂ gas.

Chemisorption capacities were measured by injecting a calibrated sample volume of CO gas (Airco, 99.99%) at 1-min intervals into an He flow (45 sccm) passing over the catalyst sample until CO uptake ceased. Prior to injection, the CO was passed through a coil of 1/8-in. stainless steel tubing submerged in a pentane slush to remove metal carbonyl impurities. Catalyst samples were maintained at a temperature of 273 K during CO chemisorption measurements.

Thiophene HDS Activity Measurements. Thiophene HDS activity measurements were carried out using an atmospheric pressure flow reactor outfitted with a gas chromatograph (HP 5890 series II). The gas chromatograph is equipped with a flame ionization detector for on-line analysis of thiophene and hydrocarbon products. The flow reactor system has been described in detail elsewhere.¹⁰ Catalyst samples (~0.10 g) were supported on a quartz wool plug located within a quartz U-tube reactor (15 mm o.d.) under a 50 sccm flow of a 1.8 mol % thiophene/H₂ mixture prepared by means of a two-stage thiophene bubbler apparatus. The thiophene used in this study (Aldrich Chemical Co., 99+%) was purified according to the procedure of Spies and Angelici¹¹ prior to use to remove thiol impurities. The reaction temperature was maintained using a ceramic-fiber furnace (Watlow) outfitted with a programmable temperature controller (Omega). Oxidic catalyst samples were degassed in a 60 sccm flow of He at 673 K for 1 h, sulfided in a flowing 3.03% H₂S/H₂ mixture (60 sccm) while heating from 298 to 623 K in 1 h and then held at 623 K for 2 h. Following sulfidation, catalyst samples were degassed again in flowing He (60 sccm) at 643 K for 10 min, and the flow was then switched to the thiophene/H₂ mixture. Thiophene HDS conversion data were collected at 1-h intervals over 24 h at a reaction temperature of 643 K. Steady-state conversion was achieved after 16–20 h; catalyst activities reported here are the values after 24 h on stream. The major HDS products (1,3-butadiene, 1-butene, *cis*-2-butene, *trans*-2 butene, and butane) and unreacted thiophene were separated using a 30-m GS-Alumina column (J & W Scientific). C₁–C₃ hydrocarbons totaled <1% of the products. The detector response for the C₄ hydrocarbon products was calibrated with analytical gas standards (Scott) to facilitate conversion calculations.

Infrared Spectroscopy and Temperature Programmed Desorption Measurements. IR spectroscopic and TPD experiments were carried out in a bakeable, stainless steel ultrahigh vacuum (UHV) chamber. The chamber is pumped by a 110 L/s ion pump and is also equipped with a high-pressure cell that can be isolated from the vacuum chamber. The system has been described in detail elsewhere.¹²

IR measurements were carried out in the transmission mode over the 4000–1000 cm⁻¹ range using a Mattson RS-1 FTIR spectrometer equipped with a narrow-band MCT detector. The FTIR spectrometer is interfaced to a personal computer for data acquisition and subsequent treatment. For TPD experiments, the

UHV system is outfitted with a Leybold-Inficon Quadrex 200 quadrupole mass spectrometer capable of monitoring six masses simultaneously; the mass spectrometer is also interfaced to a personal computer for data acquisition and treatment.

The procedure for mounting samples in the UHV system has been described in detail elsewhere.¹² Approximately 5.0 mg of γ -Al₂O₃ or of an alumina-supported metal oxide precursor was pressed at ~10 000 psi into a nickel metal mesh (50 × 50 mesh size, 0.002 in. wire diameter); the area of the pressed samples was 0.80 cm². The temperature of the sample was monitored by means of a chromel–alumel thermocouple spot-welded to the nickel mesh. Following mounting in the UHV system, the catalyst samples were evacuated to 10⁻³ Torr over a period of ~30 min. Sulfided catalysts were synthesized from oxidic catalysts via two consecutive sulfidation treatments consisting of heating to 623 K in 100 Torr of a 3.03% H₂S/H₂ mixture for 30 min. Following sulfidation, the catalyst samples were reduced in a 60 sccm flow of H₂ at 573 K (Cu/Al₂O₃ and Rh/Al₂O₃) or 623 K (Mo/Al₂O₃) for 1 h. Samples of sulfided γ -Al₂O₃ were prepared in an identical fashion.

Following in situ sulfidation and reduction, the sulfided catalysts were degassed at room temperature overnight (~14 h). The typical system base pressure following such a procedure was ~5.0 × 10⁻⁹ Torr. IR measurements of adsorbed CO were used to confirm successful preparation of sulfided catalysts. Catalyst samples were exposed to 5.0 Torr (and in one case 700 Torr) of CO at 298 K, and an IR spectrum was acquired (32 scans, 4 cm⁻¹). The catalyst sample under study was then evacuated to UHV pressures and flashed to 700 K, in order, to desorb CO from the catalyst surface. Three kinds of adsorption experiments were carried out on γ -Al₂O₃ and on the sulfided Cu/Al₂O₃, Mo/Al₂O₃, and Rh/Al₂O₃ catalysts. In each case, IR spectral acquisition consisted of 1024 scans at 4 cm⁻¹ resolution and took approximately 6 min to acquire. The sample spectrum was ratioed against a background spectrum acquired using a blank nickel metal mesh mounted in the sample holder. Depending upon the experiment, the background spectrum was acquired either in UHV, in a partial pressure of thiophene, 1,3-butadiene, or 1-butene (e.g., $P_{\text{Th}} = 5.0$ Torr) or in a gas mixture of thiophene, 1,3-butadiene, or 1-butene with H₂ (e.g., $P_{\text{Th}} = 5.0$ Torr, $P_{\text{H}_2} = 277.8$ Torr). The first type of experiment investigated the adsorption of thiophene on catalyst surfaces at low temperatures. In these experiments, the catalyst sample was initially cooled to ~140 K, and an IR spectrum was acquired. Following acquisition of this predose IR spectrum, the sample was heated to 190 K, the high-pressure cell was isolated from the UHV system, and the sample was then exposed to 0.100 Torr of thiophene for 40 min. Previous work in our laboratory has shown that dosing thiophene on γ -Al₂O₃ at temperatures below 190 K results in the formation of multilayers of thiophene on the external surfaces of the alumina support.¹³ By dosing at 190 K, thiophene is able to diffuse into the pores of the γ -Al₂O₃ and to adsorb onto the internal surfaces of the metal oxide powder. In addition, a dose of 0.100 Torr of thiophene for 40 min was found to produce a saturation coverage of thiophene on the γ -Al₂O₃. The thiophene dose pressure of 0.100 Torr was measured in the 1/4-in. tubing leading from the thiophene reservoir to the high-pressure cell and not at the sample where the precise pressure is unknown. The thiophene used in these experiments was purified as described above for the thiophene HDS activity measurements as well as by repeated freeze–pump–thaw cycles. Following exposure of the catalyst samples to thiophene, the valve linking the high-pressure cell and the UHV system was opened, and the sample was cooled to ~140

TABLE 1: Surface Areas and Chemisorption Capacities

catalyst	BET surface area (m ² /g)	CO chem. capacity (μmol/g)	normalized chem. capacity
sulf. Cu/Al ₂ O ₃	195	6.8	1.0
sulf. Mo/Al ₂ O ₃	206	46.3	6.8
sulf. Rh/Al ₂ O ₃	185	74.0	10.9

K. The chamber pressure typically fell to less than 1×10^{-8} Torr within 5 min of opening the valve. An IR spectrum was then acquired at a temperature of ~ 140 K. The catalyst sample was then annealed to 200 K for 1 min and cooled to 140 K, and an IR spectrum was acquired. This procedure was repeated with the annealing temperature increased in 25 K increments until the IR absorbances associated with adsorbed thiophene could not be differentiated from the spectra's inherent background noise.

The second and third types of experiments were carried out at temperatures of 298 K and above and consisted of acquiring IR spectra in the presence of gas-phase thiophene, 1,3-butadiene, or 1-butene ($P_{\text{gas}} = 5.0$ Torr) or in a gas mixture of thiophene, 1,3-butadiene, or 1-butene and H₂ ($P_{\text{gas}} = 5.0$ Torr, $P_{\text{H}_2} = 277.8$ Torr), respectively. An IR spectrum of a sulfided catalyst sample was acquired in UHV at 298 K prior to isolating the sample from UHV and exposing it to a pure gas or gas/H₂ mixture. Following equilibration of the sample within the gas mixture, another IR spectrum was acquired. The sample was then heated in the gas mixture to 300 K and held at that temperature for 1 min. The sample was then allowed to cool to 298 K, and an IR spectrum was acquired. This procedure was repeated with the annealing temperature increased in 50 K increments up to a temperature of 700 K. Upon completion of the 700 K anneal, cooling to 298 K, and IR spectral acquisition, the high-pressure cell was evacuated, and the sample was exposed to UHV. When the pressure had decreased to 1.0×10^{-7} Torr, a TPD experiment was carried out over the temperature range of 300–700 K while typically monitoring mass-to-charge ratios of 2, 34, 41, 43, 54, and 84.

All IR spectra are reproduced without any smoothing treatment, being prepared by subtracting the IR spectrum acquired immediately prior to dosing from the IR spectrum acquired after dosing or annealing. The TPD spectra presented are also reproduced without any smoothing treatment.

Results

BET Surface Areas and CO Chemisorption Capacities.

The BET surface areas and CO chemisorption capacities for the sulfided Cu, Mo, and Rh catalysts are listed in Table 1. On the basis of the catalyst surface areas and precursor loadings, metal surface concentrations for the Cu/Al₂O₃, Mo/Al₂O₃, and Rh/Al₂O₃ catalysts are calculated to be 3.2×10^{14} , 2.9×10^{14} , and 3.3×10^{14} metal atoms/cm², respectively. Carbon monoxide adsorption site densities can also be calculated for the catalysts and are 2.1×10^{12} , 1.4×10^{13} , and 2.4×10^{13} CO molecules/cm² for the sulfided Cu/Al₂O₃, Mo/Al₂O₃, and Rh/Al₂O₃ catalysts, respectively.

Thiophene HDS Activity Measurements. Thiophene HDS activities were measured for the sulfided Cu/Al₂O₃, Mo/Al₂O₃, and Rh/Al₂O₃ catalysts at 643 K and are listed in Table 2. Under the reaction conditions used, thiophene conversion ranged from just 0.2 mol % for the sulfided Cu catalyst to 32 mol % for the sulfided Rh catalyst. The γ -Al₂O₃ support used in this study was inactive for thiophene HDS at the reaction temperature. The HDS product distributions were similar for the sulfided Mo and Rh catalysts, with butenes being the major products.

TABLE 2: Thiophene Hydrodesulfurization Activities

catalyst	HDS activity ^a (nmol thiophene g ⁻¹ s ⁻¹)	normalized HDS activity
sulf. Cu/Al ₂ O ₃	13	1.0
sulf. Mo/Al ₂ O ₃	427	32.6
sulf. Rh/Al ₂ O ₃	2133	162.8

^a Measured after 24 h at 643 K.

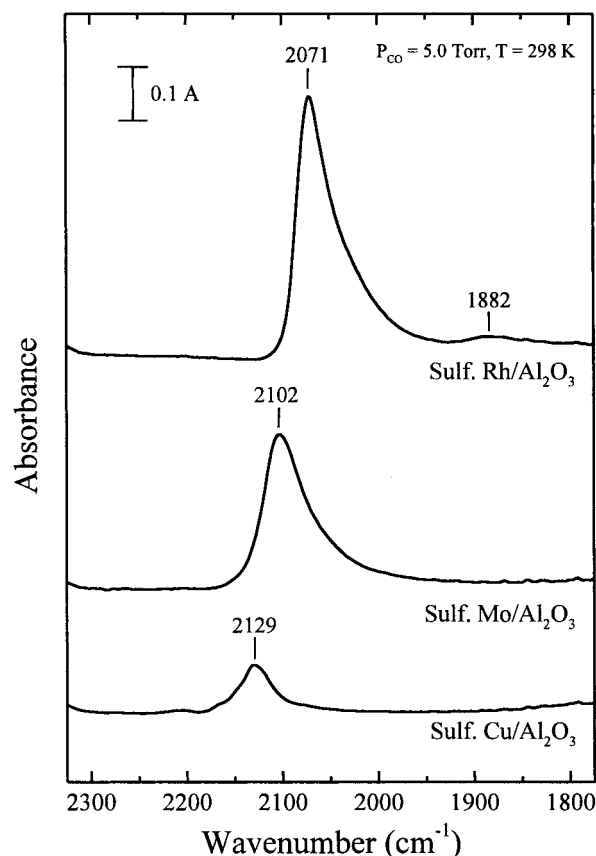


Figure 1. IR spectra of adsorbed CO on alumina-supported, sulfided Cu, Mo, and Rh catalysts. The IR spectra were acquired at 140 K in 5.0 Torr of CO.

The only major difference was that significantly more butane was produced over the sulfided Rh catalyst (17.4 mol % of products) than over the sulfided Mo catalyst (7.7 mol % of products). The only product observed for thiophene HDS over the sulfided Cu catalyst was *trans*-2-butene.

Infrared Spectroscopy Measurements of Adsorbed CO.

Shown in Figure 1 are IR spectra acquired for the sulfided Cu/Al₂O₃, Mo/Al₂O₃, and Rh/Al₂O₃ catalysts exposed to 5.0 Torr of CO at 140 K. If one assumes similar extinction coefficients for adsorbed CO on the three catalysts, then there is good qualitative agreement between the intensities of the IR absorbances in the ν_{CO} region and the CO chemisorption capacities reported in Table 1. The peak position of the ν_{CO} absorbance for the sulfided Cu/Al₂O₃ catalyst, 2129 cm⁻¹, is consistent with CO adsorption on coordinately unsaturated (cus) Cu¹⁺ sites.¹⁴ The IR spectrum for adsorbed CO on the sulfided Mo/Al₂O₃ catalyst exhibits a single absorbance at 2102 cm⁻¹, similar to what we have observed previously.¹⁵ Knözinger and co-workers¹⁶ have tentatively assigned this absorbance, observed at 2108 cm⁻¹ in their spectra, to CO bonded to cus Mo²⁺ sites. While there is agreement in the literature that this absorbance is associated with CO adsorbed on sulfur vacancies located on the edge planes of MoS₂ crystallites, there is no general agreement on the oxidation state of the Mo atoms exposed by

such vacancies. As a result, we will refer to these adsorption sites as $\text{cus Mo}^{\delta+}$ sites.

The IR spectrum of adsorbed CO on the sulfided Rh/ Al_2O_3 catalyst exhibits a large absorbance at 2071 cm^{-1} and a very weak absorbance at 1882 cm^{-1} . Rice et al.¹⁷ have reported frequency ranges for adsorbed CO on Rh/ Al_2O_3 catalysts. The peak position of the intense absorbance in our spectrum at 2071 cm^{-1} is at the high end of the range given for terminally bonded CO on Rh^0 sites ($2042\text{--}2076\text{ cm}^{-1}$) and slightly below the range reported for terminally bonded CO on Rh^{1+} sites ($2080\text{--}2100\text{ cm}^{-1}$).¹⁷ The weak absorbance at 1882 cm^{-1} is in the range for CO bridge bonded to two Rh^0 sites. We also acquired an IR spectrum (not shown) for adsorbed CO on a sulfided Rh/ Al_2O_3 catalyst at a CO pressure of 700 Torr. This spectrum is more complicated than the one displayed in Figure 1 and shows similarities to one reported by Srinivas and Chuang¹⁸ for a Rh/ Al_2O_3 catalyst sulfided at 673 K. Our higher pressure spectrum exhibits peaks at 1886, 2013, 2031, and 2081 cm^{-1} as well as a shoulder at 2065 cm^{-1} . The peak at 1886 and the shoulder at 2065 cm^{-1} are assigned to bridge and terminally bonded CO, respectively, at Rh^0 sites. The peaks at 2013 and 2081 cm^{-1} are assigned to bridge- and terminally bonded CO on Rh^{1+} sites, while the peak at 2031 cm^{-1} is assigned to the asymmetric stretch of *gem*-dicarbonyl CO species adsorbed on Rh^{1+} sites.¹⁷ An expected symmetric stretch of the *gem*-dicarbonyl species ($2096\text{--}2102\text{ cm}^{-1}$)¹⁷ is likely unresolved from the large absorbance at 2081 cm^{-1} that extends to 2125 cm^{-1} . Sulfur vacancies produced by H_2 reduction of a sulfided Rh/ Al_2O_3 catalyst at 573 K apparently expose Rh sites with oxidation states in the range of 0 to +1.

Infrared Spectroscopy Measurements of Adsorbed Thiophene at Low Temperatures. Shown in Figure 2 are IR spectra of adsorbed thiophene on sulfided Cu/ Al_2O_3 , Mo/ Al_2O_3 , and Rh/ Al_2O_3 catalysts previously dosed with thiophene at 190 K and then cooled to 140 K prior to spectral acquisition. The majority of the bands, common to each spectrum, may be assigned based upon previous analogous studies performed in our laboratory.^{13,15} Thus, similar assignments are assumed here. The IR spectrum of adsorbed thiophene on the sulfided Mo/ Al_2O_3 catalyst (14.3 wt % MoO_3) in Figure 2 is similar to the spectrum we reported earlier for thiophene on a higher loading sulfided Mo/ Al_2O_3 catalyst (27.3 wt % MoO_3).¹⁵ The only significant difference is that the shoulder at 1430 cm^{-1} is more prominent for the higher loading catalyst, which is consistent with our observation that this absorbance feature is associated with thiophene adsorbed on $\text{cus Mo}^{\delta+}$ sites and increases in intensity with increased Mo loading.¹⁵ In our earlier study, the absorbance feature at 1430 cm^{-1} was assigned to the symmetric $\text{C}=\text{C}$ stretch ($\nu(\text{C}=\text{C})$) of thiophene $\eta^1(\text{S})$ bonded to $\text{cus Mo}^{\delta+}$ sites of sulfided Mo/ Al_2O_3 catalysts.¹⁵

The IR spectrum of adsorbed thiophene on the sulfided Cu/ Al_2O_3 catalyst is similar to that of thiophene adsorbed on the $\gamma\text{-Al}_2\text{O}_3$ support;^{13,15} there are no absorbance features that can be assigned to thiophene bonded to cus Cu sites. The IR spectrum of adsorbed thiophene on the sulfided Rh/ Al_2O_3 catalyst exhibits a prominent shoulder at 1429 cm^{-1} , which is assigned to thiophene $\eta^1(\text{S})$ bonded to cus Rh sites on the surface of the catalyst.

Upon annealing of the sulfided Cu/ Al_2O_3 , Mo/ Al_2O_3 , and Rh/ Al_2O_3 catalysts dosed with thiophene to 200 K and higher in 25 K increments, only a gradual decrease in intensity of the IR features associated with adsorbed thiophene on the catalyst surfaces is observed. In each case, no absorbance features associated with thiophene are apparent in the IR spectra

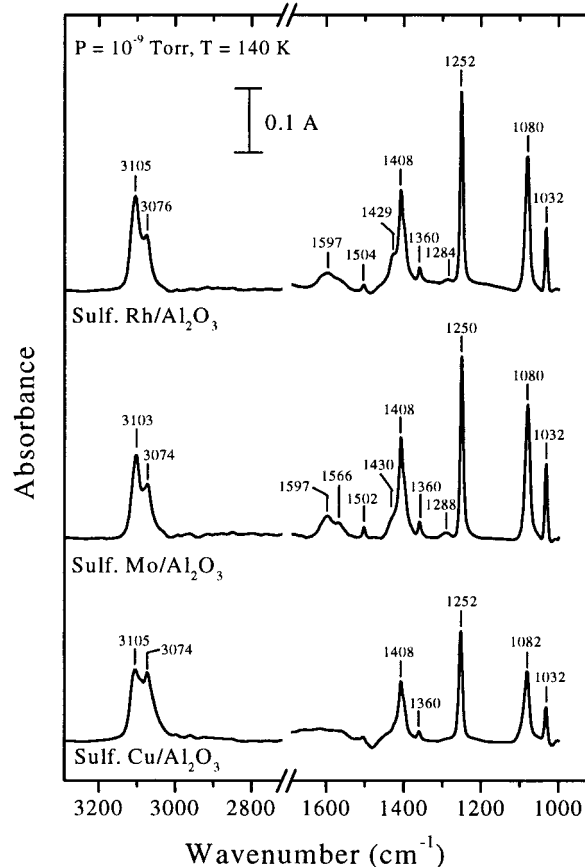


Figure 2. IR spectra of adsorbed thiophene on alumina-supported, sulfided Cu, Mo, and Rh catalysts. The IR spectra were acquired at 140 K in UHV following dosing as described in the Experimental Section.

following annealing at temperatures above 350 K. This is consistent with the results we reported previously for adsorbed thiophene on a sulfided Mo/ Al_2O_3 catalyst.¹⁵

Shown in Figure 3 are infrared spectra in the symmetric $\nu(\text{C}=\text{C})$ region of thiophene for the sulfided Cu/ Al_2O_3 , Mo/ Al_2O_3 , and Rh/ Al_2O_3 catalysts following a 225 K anneal. Common to each spectrum are absorbance features at 1401 and 1408 cm^{-1} . Both have been previously observed for thiophene adsorbed on $\gamma\text{-Al}_2\text{O}_3$, with the shoulder at 1401 cm^{-1} assigned to thiophene hydrogen-bonded to hydroxyl groups ($\text{C}_4\text{H}_4\text{S}\cdots\text{H}-\text{O}-\text{Al}$) and the peak at 1408 cm^{-1} assigned to a weakly bonded, high-coverage thiophene species whose adsorption site on the alumina surface is not known.¹³ In the IR spectrum of adsorbed thiophene on the sulfided Cu/ Al_2O_3 catalyst, there is a weak shoulder at $\sim 1424\text{ cm}^{-1}$ that can also be assigned to thiophene adsorbed on the $\gamma\text{-Al}_2\text{O}_3$ support, in this case thiophene bonded via its sulfur atom to cus Al^{3+} sites.¹³ For the sulfided Mo/ Al_2O_3 and Rh/ Al_2O_3 catalysts, a more intense, additional absorbance feature is observed at 1429 cm^{-1} . We previously showed that this absorbance feature of adsorbed thiophene increases in intensity with increasing Mo loading for a series of sulfided Mo/ Al_2O_3 catalysts.¹⁵ Furthermore, this absorbance could be suppressed if a sulfided Mo/ Al_2O_3 catalyst was dosed with CO prior to thiophene adsorption. Carbon monoxide is known to adsorb on $\text{cus Mo}^{\delta+}$ sites located on MoS_2 -like structures of sulfided Mo/ Al_2O_3 catalysts.¹⁶ The absorbance feature at 1429 cm^{-1} is most intense for adsorbed thiophene on the sulfided Rh/ Al_2O_3 catalyst and is assigned to thiophene $\eta^1(\text{S})$ coordinated to cus Rh sites on the catalyst surface.

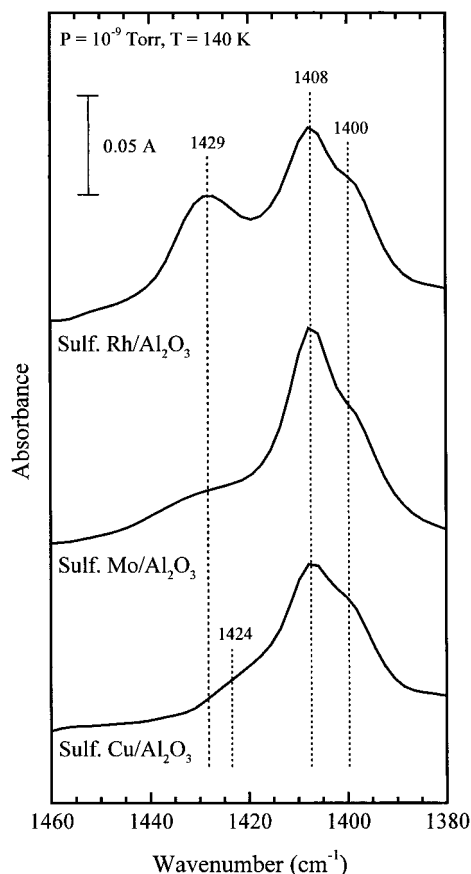


Figure 3. IR spectra in the ν_{CC} region of adsorbed thiophene on alumina-supported, sulfided Cu, Mo, and Rh catalysts. The IR spectra were acquired at 140 K in UHV following dosing as described in the Experimental Section and annealing at 225 K for 1 min.

Exposure of Catalysts to Thiophene at 300 K. The lowermost IR spectra shown in Figures 4a–6a are for sulfided Cu/Al₂O₃, Mo/Al₂O₃, and Rh/Al₂O₃ catalysts exposed to a static pressure of 5.0 Torr of thiophene at 300 K. As noted by the intensity bars in each of these figures, the spectral intensity in the ν_{CH} region has been increased by a factor of 2 so that subtle changes become more readily discernible. The IR spectra of the sulfided Cu/Al₂O₃ and Mo/Al₂O₃ catalysts in thiophene vapor alone at 300 K are similar to those of the catalysts exposed to a saturation dose of thiophene at 190 K with subsequent spectral acquisition at 140 K (see Figure 2). As for the low-temperature IR spectra, the only significant difference in the IR spectra for the sulfided Cu and Mo catalysts exposed to 5.0 Torr of thiophene from that of liquid-phase thiophene¹⁹ and thiophene adsorbed on γ -Al₂O₃¹³ is the shoulder at 1429 cm⁻¹ in the spectrum for the sulfided Mo/Al₂O₃ catalyst. Consistent with our analysis of the low-temperature results, we assign this absorbance feature to thiophene $\eta^1(S)$ bonded to $\text{cus Mo}^{\delta+}$ sites of MoS₂-like structures of the sulfided Mo catalyst. The fact that no absorbance feature is observed at 1429 cm⁻¹ in the IR spectrum of the sulfided Cu/Al₂O₃ catalyst exposed to 5.0 Torr of thiophene at 300 K is also consistent with our low-temperature results. The weak absorbance feature at 2960 cm⁻¹ in the IR spectrum of the sulfided Cu/Al₂O₃ and Mo/Al₂O₃ catalysts in thiophene vapor alone at 300 K is most likely due to trace thiol impurities and/or to a small amount of thiophene decomposition. In experiments whose results are not shown here, annealing sulfided Cu/Al₂O₃ and Mo/Al₂O₃ catalysts in 5.0 Torr of thiophene vapor in 50 K increments over the range of 300–700 K for 1 min at each temperature produced insignificant

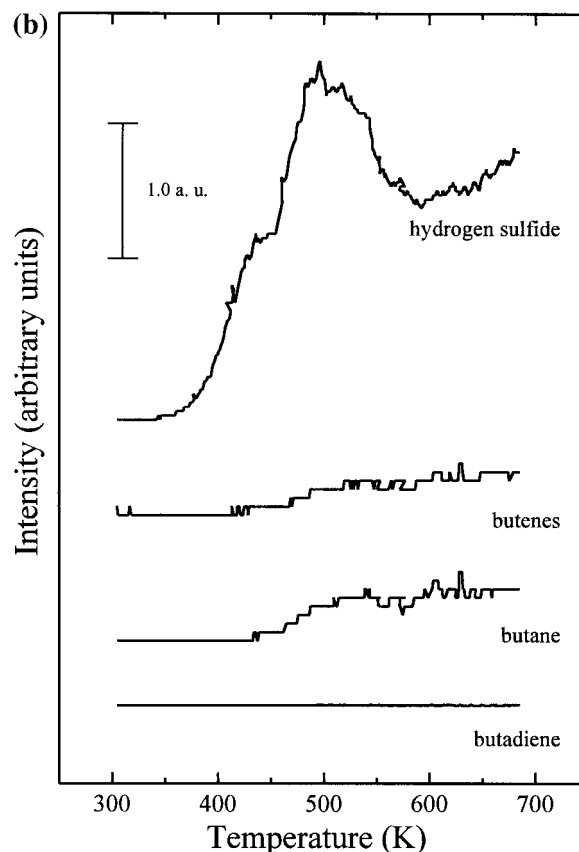
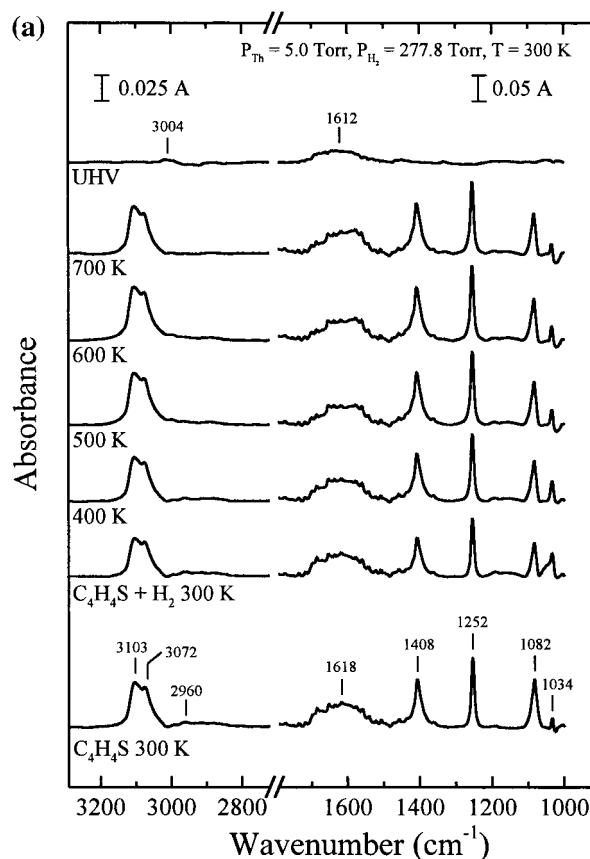


Figure 4. (a) IR spectra for a sulfided Cu/Al₂O₃ catalyst annealed at the listed temperatures for 1 min in a thiophene/H₂ mixture ($P_{Th} = 5.0$ Torr, $P_{H_2} = 277.8$ Torr). The IR spectra were acquired at 300 K. (b) TPD spectra for a sulfided Cu/Al₂O₃ catalyst following acquisition of the UHV IR spectrum shown in Panel a.

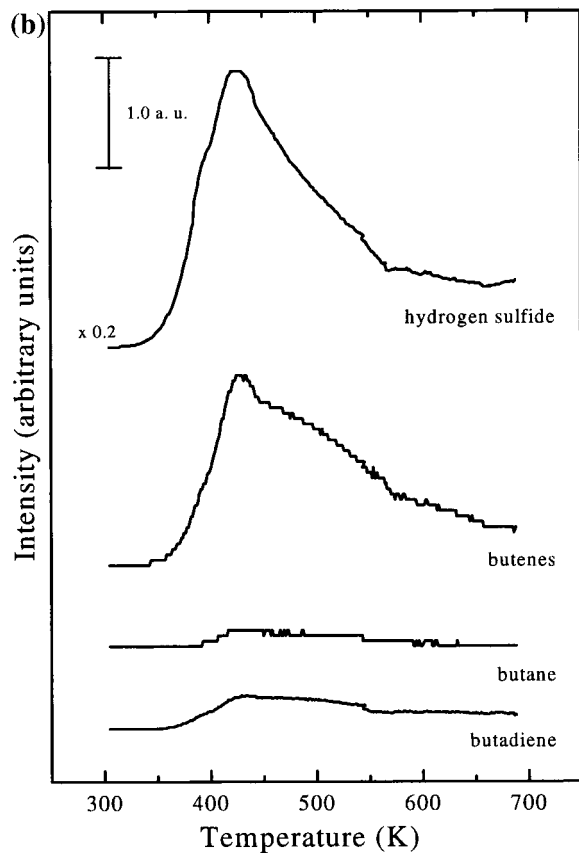
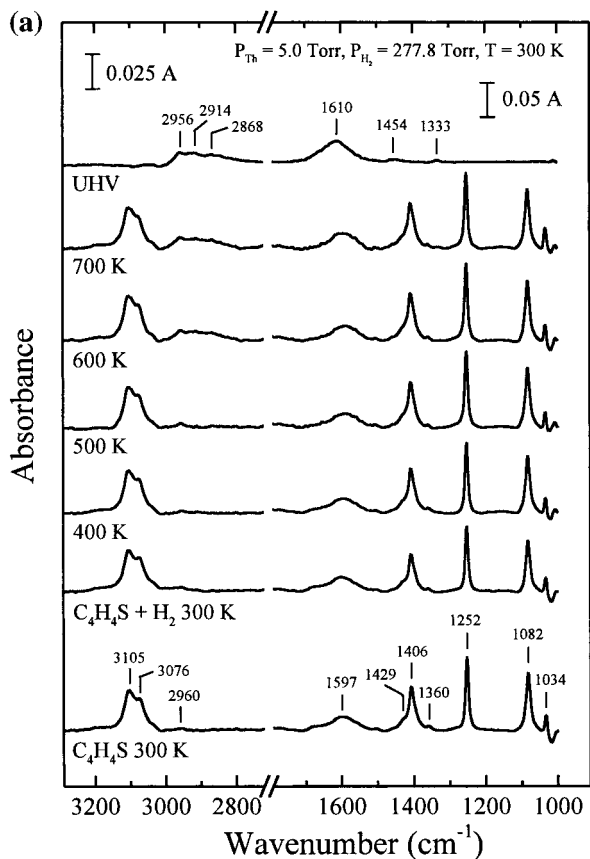


Figure 5. (a) IR spectra for a sulfided Mo/Al₂O₃ catalyst annealed at the listed temperatures for 1 min in a thiophene/H₂ mixture ($P_{\text{Th}} = 5.0$ Torr, $P_{\text{H}_2} = 277.8$ Torr). The IR spectra were acquired at 300 K. (b) TPD spectra for a sulfided Mo/Al₂O₃ catalyst following acquisition of the UHV IR spectrum shown in Panel a.

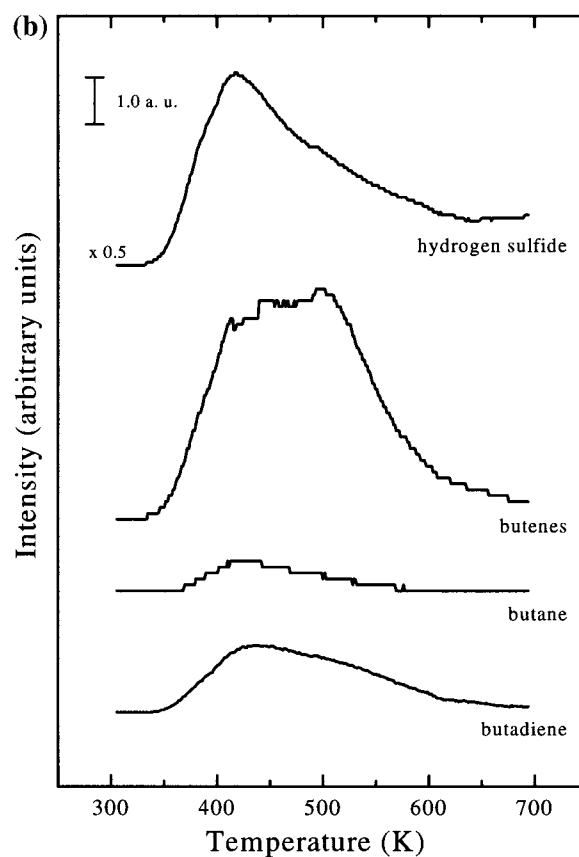
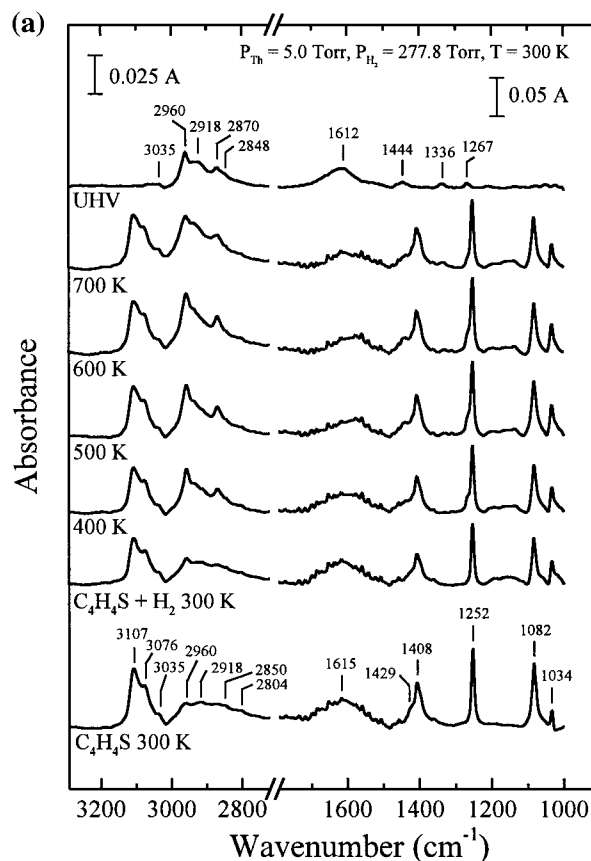


Figure 6. (a) IR spectra for a sulfided Rh/Al₂O₃ catalyst annealed at the listed temperatures for 1 min in a thiophene/H₂ mixture ($P_{\text{Th}} = 5.0$ Torr, $P_{\text{H}_2} = 277.8$ Torr). The IR spectra were acquired at 300 K. (b) TPD spectra for a sulfided Rh/Al₂O₃ catalyst following acquisition of the UHV IR spectrum shown in Panel a.

changes in the IR spectra acquired following cooling from the anneal temperature to room temperature.

In contrast to what was observed for the sulfided Cu and Mo catalysts, an IR spectrum (Figure 6a) acquired following exposure of a sulfided Rh/Al₂O₃ catalyst to 5.0 Torr of thiophene at 300 K indicates the presence of not only adsorbed thiophene but also substantial amounts of decomposition products on the catalyst surface. Consistent with the IR spectrum of a saturation coverage of thiophene on a sulfided Rh/Al₂O₃ catalyst acquired at 140 K, there is a significant absorbance feature at 1429 cm⁻¹ which is assigned to thiophene η^1 (S) bonded to cus Rh sites on the catalyst surface. In the ν_{CH} region, peaks at 3076 and 3107 cm⁻¹ are assigned to adsorbed thiophene, while a band of absorbance features in the range of 2800–3000 and a peak at 3035 cm⁻¹ are assigned to decomposition products. The new absorbance features observed in the 2800–3000 cm⁻¹ range are similar to those observed by Yates and co-workers²⁰ for a reduced 10 wt % catalyst exposed to 1,3-butadiene at 300 K. Consistent with this work,²⁰ the following assignments are made in the ν_{CH} region: 2850 [$\nu_{\text{s}}(\text{CH}_2)$], 2918 [$\nu_{\text{as}}(\text{CH}_2)$], 2960 [$\nu_{\text{as}}(\text{CH}_3)$], and 3035 cm⁻¹ [$\nu_{\text{as}}(\text{=CH})$]. The weak absorbance feature at 2804 cm⁻¹ may be due to an overtone band. In an experiment whose results are not shown here, annealing a sulfided Rh/Al₂O₃ catalyst in 5.0 Torr of thiophene vapor in 50 K increments over the range of 300–700 K for 1 min at each temperature produced little change from the IR spectrum shown at the bottom of Figure 6a. Following the 700 K anneal, the sulfided Rh catalyst was cooled to 298 K and was exposed to UHV, and IR and TPD spectrum were acquired. The IR spectrum exhibited weak absorbance features at 1520, 2860, 2918, and 2962 cm⁻¹. Subsequent acquisition of a TPD spectrum revealed small desorption peaks for butadiene and butenes.

Exposure of Catalysts to Thiophene/H₂ at High Temperatures. Following thiophene exposure ($P_{\text{Th}} = 5.0$ Torr) at 300 K and acquisition of the bottommost IR spectra shown in Figures 4a–6a, 277.8 Torr of H₂ was added in each case to the high-pressure cell for the sulfided Cu/Al₂O₃, Mo/Al₂O₃ and Rh/Al₂O₃ catalysts. The composition of the resulting thiophene/H₂ mixture (1.8 mol % thiophene) is the same as that employed in the HDS flow reactor measurements. The catalyst samples were annealed for 1 min to increasing temperatures in 50 K increments over the range of 300–700 K, followed by IR spectral acquisition after cooling to room temperature. As shown in Figure 4a, annealing the sulfided Cu/Al₂O₃ catalyst in the thiophene/H₂ mixture produces only slight changes in the IR spectra. By 500 K, the very weak absorbance feature at 2960 cm⁻¹ has disappeared. Evacuation following the 700 K anneal reveals two weak absorbance features at 1612 and 3004 cm⁻¹. Shown in Figure 4b is the TPD spectrum corresponding to the “UHV” IR spectrum for the sulfided Cu spectrum; this spectrum exhibits only small desorption features associated with butenes, butane, and H₂S.

IR spectra acquired after annealing a sulfided Mo/Al₂O₃ catalyst in a thiophene/H₂ mixture (Figure 5a) show more substantial changes than were observed for the sulfided Cu/Al₂O₃ catalyst. Absorbance features in the ν_{CH} region are observed to grow as the anneal temperature is increased to 500 K and higher. Following evacuation to UHV after the 700 K anneal, absorbance features associated with thiophene disappear, while peaks at 1333 [$\rho_{\text{w}}(\text{CH}_2)$], 1454 [$\delta(\text{CH}_3)$], 1610 [$\nu(\text{C}=\text{C})$], 2868 [$\nu_{\text{s}}(\text{CH}_3)$], 2914 [$\nu_{\text{as}}(\text{CH}_2)$], 2956 [$\nu_{\text{as}}(\text{CH}_3)$], and 3045 cm⁻¹ [$\nu_{\text{as}}(\text{=CH})$] remain essentially unchanged. Assignment of these absorbances was based upon the Yates study²⁰ discussed above; the work of Trombetta et al.,²¹ who examined the

adsorption of butenes on γ -Al₂O₃; and the results of Campione and Ekerdt,²² who investigated the adsorption of 1-butene on a reduced Ni/SiO₂ catalyst. The TPD spectrum acquired following the UHV IR measurement is shown in Figure 5b and exhibits desorption peaks for butadiene, butenes, butane, and H₂S that are significantly greater in magnitude than for the sulfided Cu/Al₂O₃ catalyst annealed under similar conditions. Butene desorption is the most significant of the C₄ hydrocarbons and exhibits a maximum rate of desorption at 430 K with a high-temperature shoulder at \sim 500 K. A significant amount of butadiene is also observed to desorb from the surface with a maximum rate of desorption at \sim 440 K. Both the absorbance features in the UHV IR spectrum and the desorption peaks in the subsequently acquired TPD spectrum are similar to but weaker in intensity than those observed for a sulfided Mo/Al₂O₃ catalyst annealed at 693 K in a higher pressure thiophene/H₂ mixture ($P_{\text{Th}} = 9.5$ Torr, $P_{\text{H}_2} = 490.5$ Torr) for a total of 70 min.¹⁵ In addition to the C₄ hydrocarbon desorption peaks, a substantial H₂S desorption peak is observed with a maximum rate of desorption at 426 K.

For the sulfided Rh/Al₂O₃ catalyst, addition of 277.8 Torr of H₂ to the 5.0 Torr of thiophene already in the high-pressure cell caused readily observable changes in the IR spectrum acquired at 300 K. The absorbance feature at 2960 cm⁻¹ increases in intensity relative to the other absorbances in the 2800–3000 cm⁻¹ region. Annealing the sulfided Rh/Al₂O₃ catalyst in the thiophene/H₂ mixture to 400 K resulted in a significant growth of the absorbances in the 2800–3000 cm⁻¹ region, particularly the absorbance features at 2870 and 2958 cm⁻¹. Further annealing up to 600 K leads to additional IR intensity growth in the 2800–3000 cm⁻¹ region, followed by a slight decrease following a 700 K anneal. Evacuation to UHV causes the IR absorbances for thiophene, which is weakly chemisorbed to the catalyst surface, to disappear. As indicated by IR absorbances at 1267, 1336, 1444, 1612, 2848, 2870, 2918, 2960, and 3035 cm⁻¹, however, one or more strongly adsorbed species remain on the surface following evacuation to UHV. Drawing again upon studies of adsorbed 1,3-butadiene and butenes on catalyst surfaces,^{20–23} the following assignments can be made: 1267 [$\rho_{\text{r}}(\text{CH}_2)$], 1336 [$\rho_{\text{w}}(\text{CH}_2)$], 1444 [$\delta(\text{CH}_2)$], 1612 [$\nu(\text{C}=\text{C})$], 2848 [$\nu_{\text{s}}(\text{CH}_2)$], 2870 [$\nu_{\text{s}}(\text{CH}_3)$], 2918 [$\nu_{\text{as}}(\text{CH}_2)$], 2960 [$\nu_{\text{as}}(\text{CH}_3)$], and 3035 cm⁻¹ [$\nu_{\text{as}}(\text{=CH})$]. The TPD spectrum acquired after obtaining the UHV IR spectrum shows desorption features for butadiene, butenes, butane, and H₂S. For butenes, two desorption features are observed with maximum rates of desorption at 450 and 500 K. Maximum rates of butadiene, butane, and H₂S desorption are observed at 440, 430, and 418 K, respectively. Consistent with the IR spectra, the C₄ hydrocarbon desorption peaks are dramatically larger for the sulfided Rh/Al₂O₃ catalyst than was observed for the sulfided Cu/Al₂O₃ and Mo/Al₂O₃ catalysts. In contrast, the H₂S desorption peak is significantly smaller for the sulfided Rh catalyst when compared to the sulfided Mo catalyst. In comparing the TPD spectra in Figures 4b–6b, it is important to note the different intensity bars in the figures.

Exposure of Catalysts to 1,3-Butadiene and 1-Butene at 300 K. To aid in the interpretation of the IR and TPD spectra for catalysts exposed to thiophene and thiophene/H₂ mixtures, similar experiments were carried out for sulfided Rh/Al₂O₃ catalysts exposed to 1,3-butadiene and 1-butene alone and with H₂ (see following section). Shown at the bottom of Figure 7a is the IR spectrum of a sulfided Rh/Al₂O₃ catalyst exposed to 5.0 Torr of 1,3-butadiene at 300 K. Absorbance features are observed at 1026, 1199, 1288, 1379, 1435, 1587, 1633, 2914,

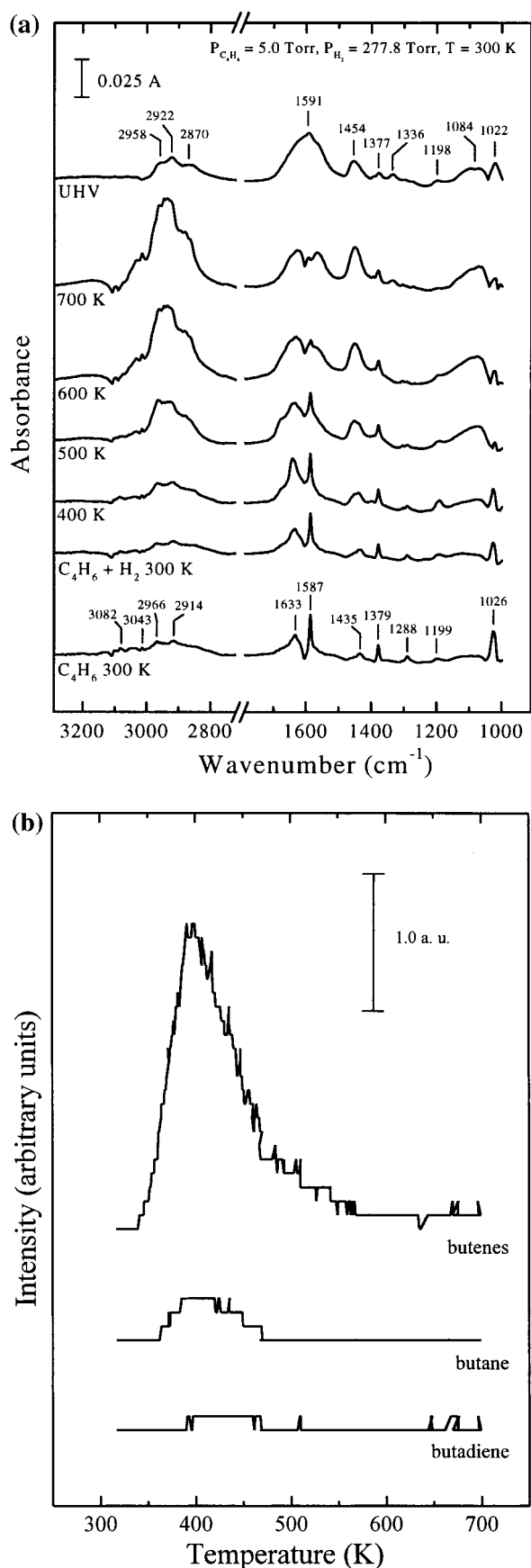


Figure 7. (a) IR spectra for a sulfided Rh/Al₂O₃ catalyst annealed at the listed temperatures for 1 min in a 1,3-butadiene/H₂ mixture ($P_{\text{C}_4\text{H}_6} = 5.0$ Torr, $P_{\text{H}_2} = 277.8$ Torr). The IR spectra were acquired at 300 K. (b) TPD spectra for a sulfided Rh/Al₂O₃ catalyst following acquisition of the UHV IR spectrum shown in Panel a.

2966, 3043, and 3082 cm⁻¹. This IR spectrum shows significant differences from that of the γ -Al₂O₃ support exposed to 1,3-butadiene under the same conditions which only exhibits bands indicative of molecularly adsorbed species. The IR spectrum at the bottom of Figure 7a instead shows similarities to those obtained by Yates and co-workers^{20,23} for a Rh/Al₂O₃ catalyst exposed to 1,3-butadiene at 200 K or below, followed by warming to 300 K. Focusing on the ν_{CH} region, the low intensity of absorbance features at 3043 and 3082 cm⁻¹ relative to those at 2914 and 2966 cm⁻¹ indicates that significant rehybridization of carbon atoms from sp² to sp³ has occurred in the adsorbed hydrocarbon layer.

Shown at the bottom of Figure 8a is an IR spectrum for a sulfided Rh/Al₂O₃ catalyst exposed to 5.0 Torr of 1-butene at 300 K. This spectrum is quite similar to the one we acquired for γ -Al₂O₃ exposed to 5.0 Torr of 1-butene at 300 K and to the IR spectrum acquired by Trombetta et al.²¹ for γ -Al₂O₃ exposed to 10.0 Torr of 1-butene, also at 300 K. Trombetta et al.²¹ assigned this spectrum to molecularly adsorbed 1-butene, in which there is a hydrogen bond between a hydrogen atom of a surface hydroxyl group and the adsorbate's double bond. For the sulfided Rh/Al₂O₃ catalyst investigated in our study, it is likely that there is also a significant amount of 1-butene molecularly adsorbed to cus Rh sites on the catalyst surface. Thus, assignments analogous to those of Trombetta et al.²¹ are made for the absorbance features observed in our spectrum: 1076 [$\nu(\text{C}-\text{C})$], 1379 [$\delta_{\text{s}}(\text{CH}_3)$], 1442 [$\delta(\text{=CH}_2)$], 1463 [$\delta_{\text{as}}(\text{CH}_3)$], 1630 [$\nu(\text{C}=\text{C})$], 2877 [$\nu_{\text{s}}(\text{CH}_3)$], 2939 [$\nu_{\text{as}}(\text{CH}_2)$], 2970 [$\nu_{\text{as}}(\text{CH}_3)$], and 3076 cm⁻¹ [$\nu_{\text{as}}(\text{=CH}_2)$].^{21,22,24}

Exposure of Catalysts to 1,3-Butadiene/H₂ and 1-Butene/H₂ at High Temperatures. Following exposure of sulfided Rh/Al₂O₃ catalysts to either 1,3-butadiene or 1-butene at 300 K and acquisition of the bottommost IR spectra shown in Figures 7a–8a, 277.8 Torr of H₂ was added to the high-pressure cell. Negligible change is observed in the IR spectrum of the sulfided Rh/Al₂O₃ catalyst exposed to the 1,3-butadiene/H₂ mixture at 300 K when compared to the spectrum in 1,3-butadiene alone. Annealing to 400 K and higher temperatures for 1 min followed by cooling to 300 K results in a dramatic increase in IR intensity of the bands in the ν_{CH} region associated with sp³ hybridized carbon atoms (2800–3000 cm⁻¹), indicating that hydrogenation of the adsorbed hydrocarbon layer has occurred. Evacuation to UHV results in a significant decrease in absorbance in the ν_{CH} region, particularly in the 2800–3000 region, indicating that substantial desorption of hydrocarbons from the sulfided Rh catalyst occurs at 300 K. The UHV IR spectrum shows absorbance features at 1022, ~1084, 1198, 1336, 1377, 1454, 1591, 2870, 2922, and 2958 cm⁻¹. The peak positions and spectral intensities in the ν_{CH} region are nearly identical to those observed by Yates and co-workers²⁰ for a C₄H₆-derived adlayer on a Rh/Al₂O₃ catalyst heated to 300 K in ~50 Torr of H₂. Peak assignments in the ν_{CH} region are as follows: 2870 [$\nu_{\text{s}}(\text{CH}_3)$], 2922 [$\nu_{\text{as}}(\text{CH}_2)$], 2958 [$\nu_{\text{as}}(\text{CH}_3)$]; the peak at 2870 cm⁻¹ is quite broad and likely contains an unresolved $\nu_{\text{s}}(\text{CH}_2)$ absorbance at ~2855 cm⁻¹, as observed by Yates and co-workers.²⁰ Elsewhere in the spectrum, there is a strong absorbance feature at 1591 cm⁻¹ which is assigned to a $\nu(\text{C}=\text{C})$ mode. As will be discussed in detail shortly, this peak position is at a lower frequency than was observed in the UHV spectrum derived from thiophene/H₂ (1612 cm⁻¹) and 1-butene/H₂ (1610 cm⁻¹) mixtures. The TPD spectrum, acquired after UHV IR spectral collection for the sulfided Rh/Al₂O₃ catalyst annealed in the 1,3-butadiene/H₂ mixture, is shown in Figure 7b. Butadiene, butenes, and butane are observed to desorb from

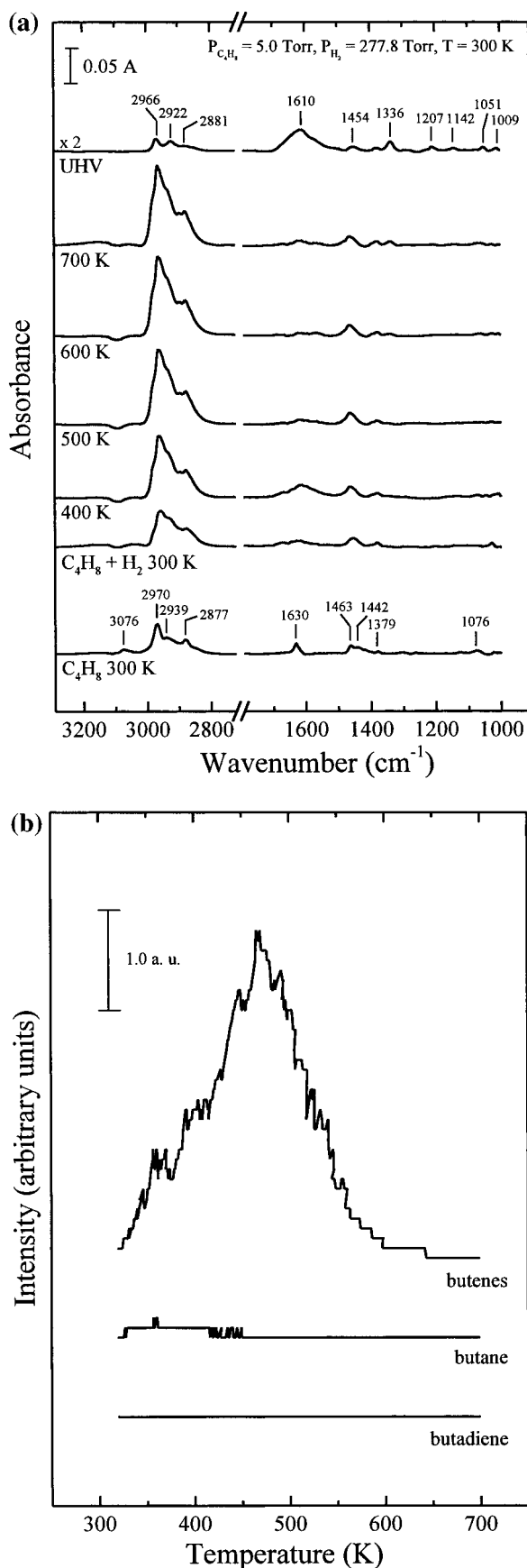


Figure 8. (a) IR spectra for a sulfided Rh/Al₂O₃ catalyst annealed at the listed temperatures for 1 min in a 1-butene/H₂ mixture ($P_{\text{C}_4\text{H}_8} = 5.0$ Torr, $P_{\text{H}_2} = 277.8$ Torr). The IR spectra were acquired at 300 K. (b) TPD spectra for a sulfided Rh/Al₂O₃ catalyst following acquisition of the UHV IR spectrum shown in Panel a.

the catalyst surface, although in significantly smaller amounts than was observed from a sulfided Rh catalyst treated similarly in a thiophene/H₂ mixture (see Figure 6b). This may be because a large amount of hydrocarbons desorbed from the sulfided Rh/Al₂O₃ catalyst immediately upon exposure to UHV, which was not the case for the sulfided Rh catalyst treated in the thiophene/H₂ mixture. The maximum rates of butadiene, butenes, and butane desorption occur at 430, 405, and 400 K, respectively.

In contrast to what was observed for 1,3-butadiene, the IR spectrum acquired for a sulfided Rh/Al₂O₃ catalyst in the presence of 5.0 Torr of 1-butene shows noticeable changes upon addition of 277.8 Torr of H₂ to the high-pressure cell. The 300 K spectrum in Figure 8a shows significant intensity growth in the ν_{CH} region when compared to the 300 K spectrum of the catalyst in 1-butene alone. Annealing the sulfided Rh catalyst to 400 K or higher for 1 min results in further intensity increases in the ν_{CH} region with much of this absorbance intensity being lost upon evacuation following the 700 K anneal. The UHV spectrum has been multiplied by a factor of 2, and its intensity scale is similar to that of the UHV spectrum in Figure 7a. The following assignments are made: 1009 [$\rho_r(\text{CH}_3)$], 1051 [$\nu(\text{C}-\text{C})$], 1142 [$\rho_w(\text{CH}_3)$], 1207 [$\rho_r(\text{CH}_2)$], 1336 [$\rho_w(\text{CH}_2)$], 1454 [$\delta(\text{CH}_2)$], 1610 [$\nu(\text{C}=\text{C})$], 2881 [$\nu_s(\text{CH}_3)$], 2922 [$\nu_{\text{as}}(\text{CH}_2)$], and 2966 cm⁻¹ [$\nu_{\text{as}}(\text{CH}_3)$].^{21,22,24,25} Shown in Figure 8b is the TPD spectrum acquired after the UHV IR spectrum. Insignificant amounts of butadiene and butane desorb from the surface of the sulfided Rh/Al₂O₃ catalyst, while a large butene desorption peak with a maximum rate of desorption is observed at 470 K.

Discussion

At the most basic level, the HDS activity of a given transition metal sulfide is the product of the sulfide catalyst's active site density and the HDS activity per site (i.e., the catalyst's turnover frequency). In this study, we have investigated both the catalytic and fundamental surface chemical properties of thiophene HDS over transition metal sulfide catalysts with low (sulfided Cu/Al₂O₃), medium (sulfided Mo/Al₂O₃), and high (sulfided Rh/Al₂O₃) HDS activity. Reference to Table 2 reveals substantial differences in the thiophene HDS activities of the sulfided Cu, Mo, and Rh catalysts as measured in our laboratory; the trend is similar to that reported previously for the same sulfided transition metals supported on high surface area carbon. From the results of Ledoux et al.,³ relative thiophene HDS activities of 1:64:6800 can be calculated for highly dispersed, sulfided Cu, Mo, and Rh supported on carbon, respectively, at a reaction temperature of 623 K. Prins and co-workers² found a sulfided Rh/C catalyst to be 9 times more active than a sulfided Mo/C catalyst at 673 K for metal loadings similar to ours. Finally, Mangnus et al.²⁶ measured relative thiophene HDS activities of 1.0:3.6:6.3 at 623 K for sulfided Cu/Al₂O₃, Mo/Al₂O₃, and Rh/Al₂O₃ catalysts with loadings in the range of $(1.9-2.0) \times 10^{14}$ metal atoms/cm².

Carbon monoxide chemisorption, measured at 273 K, was used to estimate the active site density of the sulfided Cu/Al₂O₃, Mo/Al₂O₃, and Rh/Al₂O₃ catalysts (see Table 1). As discussed in the Results section, IR spectra of adsorbed CO on the sulfided Cu, Mo, and Rh catalysts reveal that CO adsorbs on cus sites on the supported metal sulfide particles; these sites are believed to be the active sites for thiophene HDS.²⁷ The CO chemisorption data, along with thiophene HDS activities measured in an atmospheric pressure flow reactor, have been used to estimate turnover frequencies for the sulfided Cu, Mo, and Rh catalysts (see Table 3). A clear trend is evident for the site densities and turnover frequencies of the three transition metal sulfides when

TABLE 3: Thiophene Hydrodesulfurization Activities

catalyst	HDS turnover frequency (s^{-1})	normalized turnover frequency
sulf. Cu/ Al_2O_3	0.0019	1.0
sulf. Mo/ Al_2O_3	0.0092	4.8
sulf. Rh/ Al_2O_3	0.0288	15.2

supported on $\gamma\text{-Al}_2\text{O}_3$; both increase in the following order: sulfided Cu < sulfided Mo < sulfided Rh. As a result, the analogous trend in thiophene HDS activities cannot be explained in terms of either the site density or the turnover frequencies alone. The catalyst with the highest HDS activity, sulfided Rh/ Al_2O_3 , has the highest site density *and* turnover frequency, while the catalyst with the lowest HDS activity, sulfided Cu/ Al_2O_3 , has the lowest site density *and* turnover frequency. As reviewed in the Introduction, the HDS activities of unsupported and carbon-supported transition metal sulfides have been shown to exhibit a volcano-type dependence with respect to the position of the transition metal within the periodic table.^{1–3} Our results are in agreement with elements of recent theoretical studies by Nørskov and co-workers^{7–9} as well as by Toulhoat and co-workers^{5,6} in which explanations for the volcano-type dependence are proposed. The trend of site densities we have measured for sulfided Cu, Mo, and Rh catalysts agrees with the trend Nørskov and co-workers predict based upon their calculations of metal–sulfur bond energies.⁸ Nørskov and co-workers conclude that the principal factor determining the HDS activities of transition metal sulfides is the number of sulfur vacancies (i.e., cus site density). This conclusion, however, assumes that the HDS turnover frequencies of the transition metal sulfides do not vary significantly. Our results show that the thiophene HDS turnover frequencies of sulfided Cu, Mo, and Rh catalysts vary by more than an order of magnitude, indicating that the reactivity of cus sites on transition metal sulfide catalysts is also a determining factor, as suggested by the theoretical calculations of Toulhoat et al.⁶

Our expectation is that the fundamental surface chemistry of thiophene on sulfided Cu/ Al_2O_3 , Mo/ Al_2O_3 , and Rh/ Al_2O_3 catalysts should reflect the trends in site density and turnover frequency we have identified in this study. Reference to Figures 2 and 3 clearly shows that the trend in amount of thiophene chemisorbed on cus sites exposed at the surface of sulfided Cu, Mo, and Rh catalysts mirrors the trend in site density estimated using CO chemisorption (see Table 1). Previous work in our laboratory has shown that an absorbance feature observed at 1430 cm^{-1} in the IR spectrum of thiophene adsorbed on sulfided Mo/ Al_2O_3 catalysts is associated with thiophene adsorbed on cus $\text{Mo}^{\delta+}$ sites located at the edges of MoS_2 crystallites.¹⁵ As discussed in the Results, this absorbance feature has been assigned to the symmetric $\nu(\text{C}=\text{C})$ mode of thiophene $\eta^1(\text{S})$ bonded to cus $\text{Mo}^{\delta+}$ sites.¹⁵ IR spectra acquired following exposure of sulfided Cu/ Al_2O_3 , Mo/ Al_2O_3 , and Rh/ Al_2O_3 catalysts to a saturation dose of thiophene at 190 K (Figure 2), as well as after annealing of these catalysts to 225 K for 1 min (Figure 3), explicitly show that the absorbance feature at 1429 cm^{-1} increases in relative intensity according to the trend: sulfided Cu < sulfided Mo < sulfided Rh. Since we do not know the value of the extinction coefficient associated with this absorbance, only a qualitative comparison can be made. To our knowledge, however, these results provide the first experimental evidence that the amount of adsorbed thiophene on coordinately unsaturated metal sites of three different transition metal sulfide catalysts follows the trend of thiophene HDS activities measured for the catalysts in a flow reactor.

To probe the reactivity of thiophene on sulfided Cu/ Al_2O_3 , Mo/ Al_2O_3 , and Rh/ Al_2O_3 catalysts, samples of the three catalysts were exposed to a thiophene/ H_2 mixture similar in composition to that used in the flow reactor studies and were subsequently annealed to increasing temperatures in the range of 300–700 K. Referring first to the IR spectra of the sulfided transition metal catalysts in 5.0 Torr of thiophene alone at 300 K, it is important to note that the intensity of the absorbance feature at 1429 cm^{-1} increases in intensity in a similar fashion as was observed at low temperatures. In addition, there is no evidence in the IR spectra indicating that thiophene is adsorbed to sulfur vacancies on the catalyst surfaces in a geometry other than $\eta^1(\text{S})$.

In this study, we have used the onset temperature of thiophene reaction, as determined by the observation of ν_{CH} intensity growth in the $2800\text{--}3000\text{ cm}^{-1}$ region, as a measure of thiophene reactivity on the sulfided Cu, Mo, and Rh catalysts. As we will discuss shortly, the trend in thiophene reactivity we have observed via IR spectroscopy in the well-defined conditions of our high-pressure cell is consistent with the trend in thiophene turnover frequencies for the sulfided Cu, Mo, and Rh catalysts calculated using our flow reactor data. IR spectra acquired following exposure of the sulfided catalysts to thiophene, and subsequently thiophene/ H_2 mixtures, show that the sulfided Cu, Mo, and Rh catalysts have dramatically different reactivity toward thiophene. In the case of the sulfided Rh/ Al_2O_3 catalyst, absorbance features at 2850 , 2918 , 2960 , and 3035 cm^{-1} clearly indicate that some thiophene has decomposed on the catalyst surface at 300 K in the absence of gas-phase H_2 . This strongly contrasts with what we observed for the sulfided Cu and Mo catalysts treated similarly. Other than a very weak absorbance at 2960 cm^{-1} for the sulfided Cu and Mo catalysts exposed to 5.0 Torr of thiophene, there is no evidence for reaction of thiophene on these catalysts at 300 K. Annealing to temperatures as high as 700 K for 1-min intervals produced no additional changes. In a previous study in our laboratory,¹⁵ IR spectra acquired for a sulfided Mo/ Al_2O_3 catalyst (14.3 wt % MoO_3) exposed to a higher thiophene pressure ($P_{\text{Th}} = 9.5$ Torr) and annealed to 693 K for a total accumulated time of 70 min showed no evidence for thiophene undergoing reaction on the surface.

Addition of hydrogen to the high-pressure cell already containing 5.0 Torr of thiophene and annealing to increasing temperatures resulted in negligible change in the IR spectra of the sulfided Cu catalyst for anneal temperatures as high as 700 K and the gradual growth of absorbance features in the $2800\text{--}3000\text{ cm}^{-1}$ region for the sulfided Mo catalyst starting at 500 K. For the sulfided Rh catalyst, dramatic growth of absorbance features in this same spectral range is observed already at 300 K. On the basis of the reaction onset temperatures, the trend in thiophene reactivity is observed to be the following: sulfided Cu < sulfided Mo < sulfided Rh. Since the adsorbed species associated with the absorbance features in the $2800\text{--}3000\text{ cm}^{-1}$ region are believed to be desulfurized C_4 hydrocarbon fragments, the observed trend of onset reaction temperatures reflects the transition metal sulfide catalysts' ability to break C–S bonds and not surprisingly correlates with the trend in turnover frequencies measured in the flow reactor (see Table 3).

Reference to Figures 4a–6a shows that exposure of the sulfided Cu, Mo, and Rh catalysts to UHV following the 700 K anneal does not significantly diminish the intensity of the absorbance features in the $2800\text{--}3000\text{ cm}^{-1}$ region, indicating that the adsorbed species produced via thiophene reaction are strongly bonded to the catalyst surfaces. TPD spectra acquired

following acquisition of the UHV IR spectra (Figures 4b–6b) show the desorption of C₄ hydrocarbons and H₂S from the surface. Consistent with the spectral intensities in the UHV IR spectra, the amount of C₄ hydrocarbons observed to desorb from the catalysts increases in the following order: sulfided Cu < sulfided Mo < sulfided Rh. For the sulfided Mo/Al₂O₃ and Rh/Al₂O₃ catalysts, butenes are the predominant C₄ desorption product, with smaller amounts of butadiene and butane also desorbing from the catalyst surfaces. The TPD results for the sulfided Mo/Al₂O₃ catalyst are consistent with those we obtained earlier for a sulfided Mo/Al₂O₃ catalyst annealed to 693 K in a thiophene/H₂ mixture for 70 min.¹⁵ The relative TPD product yields are also in agreement with the flow reactor studies in which butenes were observed to be the predominant products with smaller amounts of butadiene and butane also detected. On the basis of the similarities of the UHV IR spectra and the TPD peak positions and product yields, it is likely that the adsorbed C₄ hydrocarbon fragments on the sulfided Mo/Al₂O₃ and Rh/Al₂O₃ catalysts are similar. Interestingly, the relative TPD peak area ratio of C₄ hydrocarbons to H₂S is significantly different for the sulfided Mo and Rh catalysts. The H₂S peak, even when reduced by a factor of 5, is the largest of the desorption peaks for the sulfided Mo catalyst, while this is not true for the sulfided Rh catalyst even though it has been reduced by only a factor of 2. These observations suggest that removal of sulfur as H₂S is more difficult from the sulfided Mo catalyst than from the sulfided Rh catalyst. This conclusion is also supported by the fact that the maximum rate of H₂S desorption is at a somewhat higher temperature for the sulfided Mo/Al₂O₃ catalyst (426 K) than for the sulfided Rh/Al₂O₃ catalyst (418 K).

To help identify the adsorbed C₄ hydrocarbon fragments formed when sulfided Mo and Rh catalysts are annealed in thiophene/H₂ mixtures, experiments were performed in which sulfided Rh/Al₂O₃ catalysts were exposed to 5.0 Torr of 1,3-butadiene or 1-butene, either alone or in the presence of gas-phase H₂ at 300 K. The sulfided Rh catalysts were annealed in the hydrocarbon/H₂ mixtures in a similar manner as was done for the thiophene/H₂ mixtures. Focusing initially on the IR spectrum of 1,3-butadiene alone on a sulfided Rh catalyst at 300 K (see Figure 7a), the ν_{CH} absorbances in the 2800–3000 region are similar to the IR spectrum for a sulfided Rh/Al₂O₃ catalyst exposed to thiophene alone (see Figure 6a). As mentioned in the Results, Yates and co-workers²⁰ reported a similar “envelope of absorbances” for a reduced Rh/Al₂O₃ catalyst exposed to 1,3-butadiene at 300 K. In agreement with Yates and co-workers,²⁰ we assign this band of absorbances to a mixture of adsorbed hydrocarbon species in which most of the sp² carbons in the 1,3-butadiene-derived adsorbates have rehybridized to sp³ carbons. The IR spectrum in the ν_{CH} region of a sulfided Rh/Al₂O₃ catalyst exposed to 5.0 Torr of 1-butene at 300 K (see Figure 8a) is quite different, consisting of more well-defined absorbances at 2877, 2939, 2970, and 3076 cm⁻¹. These spectral features, as well as those elsewhere in the IR spectrum, are consistent with molecularly adsorbed 1-butene.

While the IR spectra in the 2800–3000 cm⁻¹ region are most similar for sulfided Rh/Al₂O₃ catalysts exposed to thiophene and 1,3-butadiene alone at 300 K (see Figures 6a and 7a), this is not true when H₂ is added to the high-pressure cell. Following addition of 277.8 Torr of H₂ and annealing to increasing temperatures in the range of 300–700 K, the intensities of absorbance features in the ν_{CH} region for the sulfided Rh/Al₂O₃ catalysts exposed to a thiophene/H₂ mixture most closely resemble those for a sulfided Rh catalyst exposed to a 1-butene/

H₂ mixture (see Figures 6a and 8a). In particular, the $\nu_s(CH_3)$ and $\nu_{as}(CH_3)$ absorbances are more prominent in the IR spectra of the sulfided Rh catalysts exposed to the thiophene/H₂ (2870 and 2960 cm⁻¹, respectively) and 1-butene/H₂ (2881 and 2966 cm⁻¹, respectively) mixtures than for the sulfided Rh catalyst exposed to the 1,3-butadiene/H₂ mixture for which the $\nu_{as}(CH_2)$ absorbance at 2922 cm⁻¹ is more prominent.

As noted earlier, evacuation of the gas phase results in only a minor decrease in spectral intensity in the 2800–3000 cm⁻¹ region for the sulfided Rh/Al₂O₃ catalyst annealed in the thiophene/H₂ mixture (see UHV spectrum in Figure 6a). In contrast, large decreases in spectral intensity are observed when the sulfided Rh catalysts exposed to the 1,3-butadiene/H₂ and 1-butene/H₂ mixtures are evacuated to UHV, indicating that significant hydrocarbon desorption occurs at 300 K (see Figures 7a and 8a). However, the ν_{CH} absorbances that remain in the UHV IR spectra show the same relative intensities as those for the sulfided Rh catalysts in the presence of each of the different gas mixtures. As a result, the strongly adsorbed hydrocarbon species present on the catalyst surfaces in UHV appear to be representative of the predominant adsorbed species formed in the presence of the different gas mixtures.

The UHV IR spectra of the sulfided Rh/Al₂O₃ catalysts annealed in 1,3-butadiene/H₂ and 1-butene/H₂ mixtures show distinct differences not only in the ν_{CH} region but also in the $\nu(C=C)$ region. The $\nu(C=C)$ absorbance is observed at 1591 cm⁻¹ in the UHV IR spectrum derived from the sulfided Rh catalyst annealed in a 1,3-butadiene/H₂ mixture, while this same absorbance appears at 1610 cm⁻¹ for the sulfided Rh catalyst annealed similarly in a 1-butene/H₂ mixture. In both cases the $\nu(C=C)$ absorbance is quite broad, and for the sulfided Rh catalyst annealed in a 1-butene/H₂ mixture a shoulder is apparent at ~1580 cm⁻¹. It is possible, therefore, that annealing sulfided Rh/Al₂O₃ catalysts in 1,3-butadiene/H₂ and 1-butene/H₂ mixtures gives rise to two or more similar adsorbed hydrocarbon species on the catalyst surfaces but in different relative ratios.

Both the absorbance intensities in the ν_{CH} region and the peak position of the $\nu(C=C)$ absorbance (1612 cm⁻¹) for the sulfided Rh catalyst annealed in a thiophene/H₂ mixture are consistent with those of the sulfided Rh catalyst annealed in a 1-butene/H₂ mixture. TPD spectra collected after acquisition of the UHV IR spectra reveal butenes to be the major desorption product for the sulfided Rh catalysts annealed in all three gas mixtures. The maximum rate of butene desorption is most similar for the sulfided Rh/Al₂O₃ catalysts annealed in the 1-butene/H₂ (maximum 470 K) and thiophene/H₂ (maximum 500 K, shoulder ~450 K) mixtures but is significantly lower for the sulfided Rh catalyst annealed in the 1,3-butadiene/H₂ mixture (maximum 400 K). A substantial amount of butadiene was also observed to desorb from the surface of the sulfided Rh catalyst annealed in the thiophene/H₂ mixture, while essentially baseline values were recorded for the catalyst samples annealed in the hydrocarbon/H₂ mixtures.

Consistent with our earlier study of the adsorption and reactions of thiophene on sulfided Mo/Al₂O₃ catalysts, the predominant adsorbed species produced by desulfurization of thiophene on sulfided Rh/Al₂O₃ catalysts appears to be a C₄H₇ fragment. Trombetta et al.²¹ have investigated the adsorption of butenes on γ -Al₂O₃ and noted the formation of strongly adsorbed species in addition to molecularly adsorbed butenes, the latter which desorbed upon evacuation. The IR spectra of the strongly adsorbed species are consistent with the UHV IR spectra shown in Figures 6a and 8a for sulfided Rh catalysts annealed in thiophene/H₂ and 1-butene/H₂ mixtures. Trombetta

et al.²¹ assigned their IR spectra to σ -bonded allyl species of C_4H_7 stoichiometry containing either internal or terminal $C=C$ bonds. The existence of two distinct C_4H_7 species was proposed on the basis that two $\nu(C=C)$ absorbances were observed at 1588 and 1615 cm^{-1} , with the former assigned to a C_4H_7 species containing a terminal $C=C$ bond and the latter assigned to a C_4H_7 species containing an internal $C=C$ bond. The $\nu(C=C)$ absorbance at 1612 cm^{-1} in the UHV IR spectrum derived from annealing a sulfided Rh catalyst in a thiophene/ H_2 mixture would indicate that the most prevalent adsorbed C_4H_7 species on the surface has an internal $C=C$ bond. Such a species could be expected to either undergo dehydrogenation to give butadiene or hydrogenation to give butenes and butane, which is consistent with the TPD spectra shown in Figure 6a for a sulfided Rh catalyst annealed in a thiophene/ H_2 mixture. The fact that similar IR and TPD spectra are obtained for the strongly adsorbed species produced on a sulfided Rh/ Al_2O_3 catalyst annealed in a 1-butene/ H_2 mixture provides further support for identification of the species as a C_4H_7 fragment.

A number of different reaction schemes have been proposed for the thiophene HDS reaction, and these have been recently summarized elsewhere.^{27,28} Direct hydrogenolysis of $C-S$ bonds to give 1,3-butadiene and adsorbed sulfur,²⁹ internal transfer of thiophene's β -hydrogens to the sulfur atom to give diacetylene and H_2S ,³⁰ and hydrogenation of thiophene to 2,3-dihydrothiophene followed by $C-S$ bond cleavage to give 1,3-butadiene and adsorbed sulfur^{31,32} are often suggested as possible reaction pathways. The fact that we do not observe reaction of thiophene when adsorbed alone on sulfided Mo/ Al_2O_3 catalysts, even when a catalyst sample is annealed to 693 K in 9.5 Torr of thiophene vapor for 70 min,¹⁵ suggests that the internal hydrogen transfer mechanism is inoperative as it should not require gas-phase H_2 . We cannot make this same conclusion for the sulfided Rh/ Al_2O_3 catalyst for which we observe reaction of thiophene alone at 300 K to produce an IR spectrum in the ν_{CH} region (see Figure 6a) similar to what we observed for a sulfided Rh catalyst exposed to 1,3-butadiene alone at 300 K (see Figure 7a). It is not clear, however, what would be the source of H atoms for hydrogenation of the resulting diacetylene species to give an adsorbed hydrocarbon species similar to that derived from 1,3-butadiene.

Two recent studies of thiophene HDS over sulfided Mo catalysts have shown 2,3- and 2,5-dihydrothiophene as well as tetrahydrothiophene to be minor products at low reaction temperatures (473–573 K).^{28,33} In both cases, the authors conclude that dihydrothiophenes and tetrahydrothiophene are likely intermediates under HDS conditions similar to those used in our flow reactor studies. The fact that we do not observe these hydrogenated thiophenes at our reaction temperature of 643 K is not surprising as they would be expected to rapidly convert C_4 reaction products. Finally, there is one unexplained observation that is deserving of further discussion. While the IR spectra of thiophene and 1,3-butadiene when adsorbed alone on a sulfided Rh/ Al_2O_3 catalyst at 300 K are similar, addition of gas-phase hydrogen leads to IR spectra for the thiophene/ H_2 mixture that more clearly resemble those for the 1-butene/ H_2 mixture. One possible explanation of this observation is that while 1,3-butadiene is produced from thiophene when adsorbed alone on a sulfided Rh/ Al_2O_3 catalyst, reaction in a thiophene/ H_2 mixture proceeds instead via dihydrothiophene to give an adsorbed butene-1-thiolate intermediate as suggested by Sullivan and Ekerdt in their HDS reaction scheme. Cleavage of the $C-S$ bond in an adsorbed butene-1-thiolate species would yield an adsorbed C_4H_7 species similar to what we have proposed above.

This species could then undergo dehydrogenation to give 1,3-butadiene or hydrogenation to produce butenes and butane. Further studies, including investigation of the surface chemistry of 2,5-dihydrothiophene and tetrahydrothiophene on sulfided Mo/ Al_2O_3 and Rh/ Al_2O_3 catalysts, are currently under way to more fully characterize the thiophene HDS mechanism.

Conclusion

The vastly different thiophene HDS activities of alumina-supported, sulfided Cu, Mo, and Rh catalysts have been traced to differences in their site densities and turnover frequencies. Both of these quantities were found to increase in the following order: sulfided Cu < sulfided Mo < sulfided Rh. Low-temperature IR spectral measurements of adsorbed thiophene on the catalyst surfaces indicate that thiophene adsorbs in an $\eta^1(S)$ geometry to cus metal sites on the sulfided Mo and Rh particles. The amount of thiophene adsorbed on cus metal sites for the catalysts increases in the same order identified for site densities estimated by CO chemisorption. Thiophene reactivity, as measured by the onset temperature for the formation of ν_{CH} absorbances in the 2800–3000 cm^{-1} region when the catalysts were annealed in a thiophene/ H_2 mixture, also follows the trend: sulfided Cu < sulfided Mo < sulfided Rh. Strongly adsorbed species produced on the sulfided Cu, Mo, and Rh catalysts during the annealing sequence were subjected to TPD experiments that yielded C_4 hydrocarbons, with the predominant product being butenes. IR and TPD measurements of 1,3-butadiene and 1-butene on sulfided Rh/ Al_2O_3 catalysts, both in the pure gas and in gas/ H_2 mixtures, provide evidence for the tentative assignment of strongly adsorbed species produced by cleavage of $C-S$ bonds in thiophene to be a σ -bonded allyl species with C_4H_7 stoichiometry.

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