

# Identification of the Adsorption Mode of Thiophene on Sulfided Mo Catalysts

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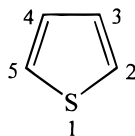
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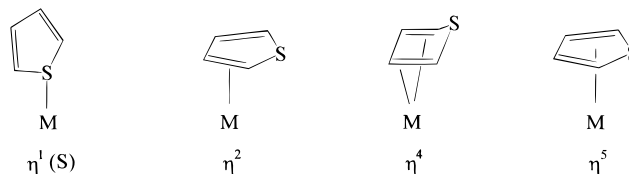
The adsorption and reactions of thiophene ( $C_4H_4S$ ) on sulfided Mo/ $Al_2O_3$  catalysts have been investigated over wide ranges of pressure ( $10^{-9}$ – $5 \times 10^2$  Torr) and temperature (140–693 K) using infrared (IR) spectroscopy and temperature-programmed desorption (TPD). When dosed at 190 K, thiophene adsorbs molecularly onto sites located on  $MoS_2$ -like structures and on uncovered alumina regions of sulfided Mo/ $Al_2O_3$  catalysts as determined by IR spectroscopy. Thiophene is weakly chemisorbed to the catalyst surface and desorbs in a single peak with a maximum rate of desorption at 243 K. Based upon interpretation of IR spectra, the adsorption mode of thiophene on the sulfided Mo portion of the catalyst surface has been determined to be  $\eta^1(S)$ , with thiophene bonded to coordinately unsaturated (cus)  $Mo^{\delta+}$  sites located on the edge planes of  $MoS_2$ -like structures. The saturation coverage of thiophene on  $MoS_2$ -like structures of a sulfided 17.6 wt % Mo/ $Al_2O_3$  catalyst is estimated to be  $C_4H_4S/Mo = 0.074$ . Thiophene is observed to become reactive on sulfided Mo/ $Al_2O_3$  catalysts only in the presence of gas-phase hydrogen and at high temperatures (i.e., 693 K). Temperature-programmed desorption in ultrahigh vacuum following heating of a sulfided 9.4 wt % Mo/ $Al_2O_3$  catalyst to 693 K in a thiophene/ $H_2$  mixture results in desorption of  $C_4$  hydrocarbons,  $H_2S$ , and  $H_2$  from the catalyst surface.

## Introduction

The selective cleavage of carbon–sulfur bonds in organo-sulfur compounds constitutes the basis for the industrially important hydrodesulfurization (HDS) process. Sulfur removal from petroleum feedstocks is accomplished by treating the organosulfur compounds with hydrogen over alumina-supported molybdenum or tungsten catalysts promoted with cobalt or nickel (e.g., Co–Mo/ $Al_2O_3$ ).<sup>1</sup> Considerable research has been carried out with the purpose of understanding the fundamental surface chemistry of the HDS process with thiophene ( $C_4H_4S$ ) most often chosen as the model organosulfur compound. These research investigations have utilized not only the techniques of heterogeneous catalysis<sup>1,2</sup> but also those of surface science,<sup>3</sup> organometallic,<sup>4</sup> and theoretical chemistry.<sup>5,6</sup>



Organometallic chemistry has provided a wealth of information concerning the bonding of thiophene to metal centers and its subsequent reactivity. Four different bonding modes have been observed for thiophene in organometallic complexes (Figure 1), and these have been suggested as possible modes for thiophene adsorption on HDS catalysts.<sup>4,7</sup> Thiophene displays reactivity in a number of different complexes, including H–D exchange,<sup>8</sup> C–S bond insertion,<sup>9</sup> and, in a few cases, hydrodesulfurization.<sup>10,11</sup> This chemistry has recently been reviewed in detail elsewhere.<sup>7,12,13</sup> Unfortunately, it has not yet been possible to isolate or observe a coordinated thiophene species that is a direct precursor to a C–S bond insertion or a



**Figure 1.** Modes of thiophene adsorption observed in transition-metal complexes.<sup>4</sup>

desulfurization product.<sup>14</sup> Indirect evidence points to  $\eta^1(S)$ -coordinated thiophene being the precursor to C–S bond cleavage,<sup>9</sup> although  $\pi$ -bonded thiophene species also undergo C–S bond cleavage when attacked by a hydride ion,<sup>15</sup> a proton,<sup>16</sup> or a base.<sup>17</sup>

Surface science studies of thiophene on single-crystal surfaces have provided insight into the HDS process as well, but they have also shown that metal single crystals are not necessarily good models for HDS catalysts. When adsorbed on the clean Mo(110)<sup>18</sup> and Mo(100)<sup>19,20</sup> surfaces in ultrahigh vacuum (UHV), for example, thiophene undergoes indiscriminate bond breaking which results in atomic carbon and sulfur on the metal surface and gaseous  $H_2$ . Preadsorbed sulfur moderates the reactivity of the molybdenum surfaces, but nonselective bond cleavage is still observed.<sup>18,19</sup> The basal plane of molybdenum disulfide ( $MoS_2$ ), on the other hand, was found to be inert to thiophene chemisorption.<sup>21</sup> Molybdenum disulfide is a layered dichalcogenide material which has a highly anisotropic structure;<sup>22</sup> macroscopic  $MoS_2$  crystals expose primarily the basal plane while active sites for HDS are thought to be located on edge planes.<sup>1</sup>

Thiophene HDS has been observed on molybdenum and rhenium single-crystal surfaces at high pressures, but no information was obtained concerning the mode of thiophene adsorption under these conditions.<sup>23–25</sup> Thiophene desulfurizes to give small amounts of butadiene on both the Pt(111)<sup>26</sup> and

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Rh(111)<sup>27</sup> surfaces and butene on the Ni(111)<sup>28</sup> surface under UHV conditions. The adsorption geometry of thiophene was found to be coverage dependent on the Pt(111) surface with thiophene  $\eta^1(\text{S})$ -bonded at high coverage and  $\eta^5$ -bonded at low coverage.<sup>26</sup> On the Rh(111) and Ni(111) surfaces, thiophene is believed to adopt  $\eta^5$  and  $\eta^1(\text{S})$  adsorption geometries, respectively, which are independent of coverage.<sup>27,28</sup>

Relatively few studies have been published in which the surface chemistry of thiophene has been investigated on unsupported MoS<sub>2</sub><sup>29–31</sup> or sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts<sup>29,31,32</sup> using vibrational spectroscopy. These studies were hindered by poor signal-to-noise ratios and/or instrumental limitations which restricted the spectral range examined. In addition, the majority of these studies were carried out at temperatures (298 K and above) at which the thiophene coverage is very low and/or utilized adsorption conditions in which we have observed thiophene to be reactive on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. On the basis of the interpretation of the vibrational spectra obtained, the authors of these studies have concluded that thiophene is  $\eta^1(\text{S})$ -bonded,<sup>31,32</sup>  $\eta^2$ -bonded,<sup>29,30</sup>  $\eta^4$ -bonded,<sup>29,30</sup> and  $\eta^5$ -bonded<sup>32</sup> to the catalyst surface.

In the current study, the surface chemistry of adsorbed thiophene on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts has been examined over wide ranges of pressure ( $10^{-9}$ – $5 \times 10^2$  Torr) and temperature (140–693 K) using the combined techniques of infrared (IR) spectroscopy and temperature-programmed desorption (TPD). By investigating thiophene adsorption on catalysts with a range of Mo loadings at low temperatures, it has been possible to identify the adsorption mode of thiophene on MoS<sub>2</sub>-like structures to be  $\eta^1(\text{S})$ . Furthermore, the conversion of thiophene to desulfurized products on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts has been observed with IR spectroscopy, and the products have been determined to be C<sub>4</sub> hydrocarbons and H<sub>2</sub>S by TPD.

## Experimental Section

**Ultrahigh-Vacuum/High-Pressure System.** The research described was carried out in a bakeable, stainless steel ultrahigh-vacuum chamber pumped by a 110 L/s ion pump and equipped with a high-pressure cell that can be isolated from the vacuum chamber; the system has been described in detail elsewhere.<sup>33</sup> In brief, the high-pressure cell consists of a 2<sup>3</sup>/<sub>4</sub> in. cube cross equipped with flange mounted CaF<sub>2</sub> windows. The sample holder is comprised of a 2<sup>3</sup>/<sub>4</sub> in. conflat flange outfitted with feedthroughs for resistive heating, temperature measurement, and liquid nitrogen cooling. The sample holder is mounted to the cell via the top face of the cube cross, perpendicular to the CaF<sub>2</sub> windows, permitting infrared measurements to be conducted in the transmission mode. Samples supported on a nickel metal mesh are clamped onto copper sample supports and can be cooled to ~140 K and heated to ~1200 K. Sample heating is accomplished using a home-built temperature controller which allows linear sample heating at rates of 0.1–10 K/s. Gases are introduced into the high-pressure cell via a welded, stainless steel gas handling system connected to the cell by 1/4 in. tubing.

**Sample Preparation and Mounting.** Oxidic precursors (MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) were prepared by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Engelhard AL-3945) with aqueous solutions of ammonium heptamolybdate (J.T. Baker Co.). Catalysts with Mo loadings of 9.4, 17.6, and 25.0 wt % were prepared; the latter two catalysts required multiple impregnations to achieve the desired Mo loading. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had a BET surface area of 255 m<sup>2</sup>/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.

Following impregnation, the catalysts were dried for 24 h at 393 K and then calcined for 3 h in air at 773 K.

The procedure for mounting samples in the ultrahigh-vacuum (UHV) system has been described in detail elsewhere.<sup>33</sup> Approximately 5.0 mg of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or of a MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> 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 cm<sup>2</sup>. 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 MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> samples were evacuated to 10<sup>−3</sup> Torr over a period of ~30 min. Sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts were synthesized from oxidic precursors via two consecutive sulfidation treatments consisting of heating to 623 K in 100 Torr (1 Torr = 133.3 N/m<sup>2</sup>) of a 3.03% H<sub>2</sub>S/H<sub>2</sub> mixture for 30 min. Following sulfidation, the catalysts were reduced in a 60 sccm/min flow of H<sub>2</sub> at 623 K for 1 h. Samples of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> used for IR-TPD studies were prepared in an identical fashion.

**IR-TPD Measurements.** Infrared measurements are accomplished using a Mattson RS-1 FTIR spectrometer that has a water-cooled source and a narrow-band MCT detector and is interfaced to a personal computer for data acquisition and 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.

Following in-situ sulfidation and reduction, sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts were degassed at room temperature overnight (~14 h). The typical system base pressure following such a procedure was ~ $5.0 \times 10^{-9}$  Torr. Combined IR-TPD measurements of adsorbed CO were used to confirm successful preparation of sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts and to estimate the number of adsorption sites on these catalysts. Depending upon the experiment, the catalyst sample was exposed to 5.0 Torr of CO at either 140 or 298 K and an IR spectrum acquired (128 scans, 4 cm<sup>−1</sup>). The catalyst sample was then evacuated to UHV pressures, an IR spectrum acquired, and a TPD experiment carried out. Carbon monoxide TPD measurements utilized a heating rate of 1 K/s while acquiring mass spectrometer data for  $m/e = 28$  up to a final temperature of 600 K. Four kinds of thiophene adsorption experiments were carried out on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. Infrared spectral acquisition consisted of 2048 scans at 4 cm<sup>−1</sup> resolution of the region 4000–1000 cm<sup>−1</sup> and took approximately 12 min to acquire. The sample spectrum was ratioed with a background spectrum acquired using a blank nickel metal mesh mounted in the sample holder. Depending upon the experiment, the background spectrum was acquired in UHV, a partial pressure of thiophene ( $P_{\text{Th}} = 9.5$  Torr) or a thiophene/H<sub>2</sub> mixture ( $P_{\text{Th}} = 9.5$  Torr,  $P_{\text{H}_2} = 490.5$  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 the predose IR spectrum, the sample was heated to 190 K, the high-pressure cell was isolated from the UHV system, and the sample was exposed to 0.100 Torr of thiophene for 40 min. Previous work in our laboratory has shown that dosing thiophene on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at temperatures below 190 K results in the formation of multilayers of thiophene on the external surfaces of the alumina support.<sup>34</sup> By dosing at 190 K, thiophene is able to diffuse into the pores of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and to adsorb onto the internal surfaces of the metal oxide powder. In addition, a dose of 0.100 Torr of thiophene for 40

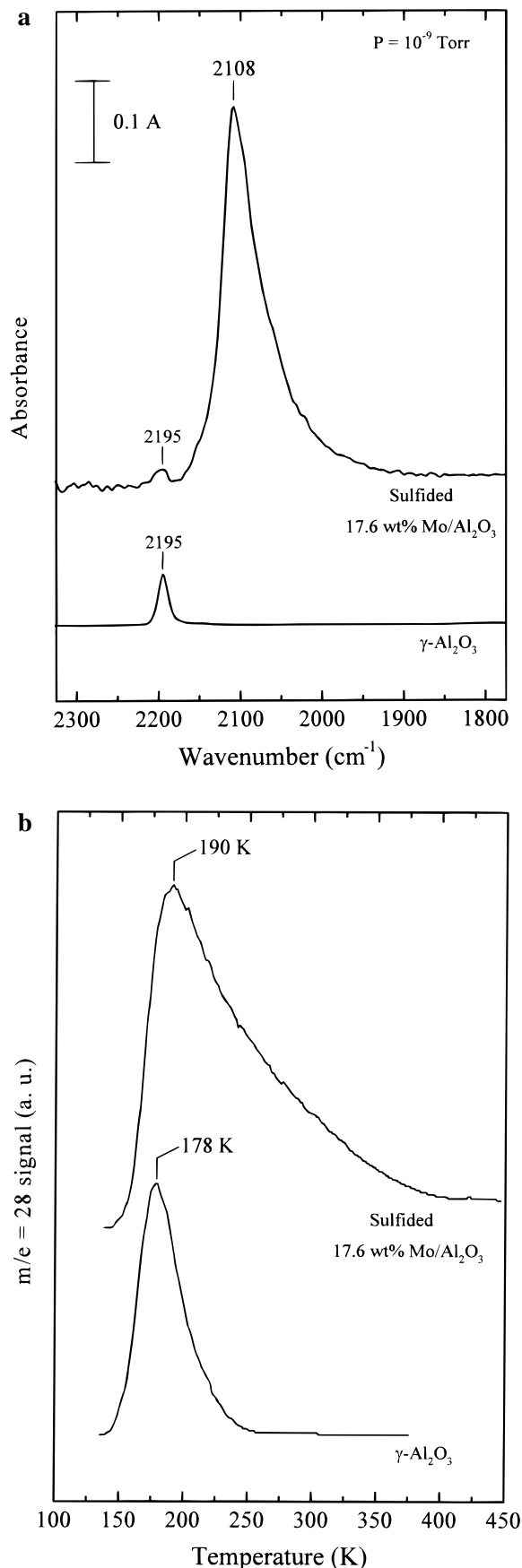
min was found to produce a saturation coverage of thiophene on the  $\gamma$ - $\text{Al}_2\text{O}_3$ . Similar results were observed for the sulfided  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts.<sup>35</sup> The thiophene dose pressure of 0.100 Torr was measured in the  $1/4$  in. tubing leading from the thiophene reservoir to the high-pressure cell and not at the sample where the pressure is unknown. The thiophene used in this study (Aldrich Chemical Co., 99+% purity) was purified according to the procedure of Spies and Angelici<sup>36</sup> 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 cooled to  $\sim 140$  K. The chamber pressure typically fell to less than  $1 \times 10^{-8}$  Torr within 5 min of opening the valve. An IR spectrum was then acquired at a temperature of  $\sim 140$  K.

Following IR spectral acquisition, a TPD experiment was carried out using a heating rate of 1 K/s while acquiring data for mass-to-charge ratios of 2 ( $\text{H}_2$ ), 34 ( $\text{H}_2\text{S}$ ), 41 ( $\text{C}_4\text{H}_8$ ), 43 ( $\text{C}_4\text{H}_{10}$ ), 54 ( $\text{C}_4\text{H}_6$ ), and 84 ( $\text{C}_4\text{H}_4\text{S}$ ) at a sampling frequency of 2 points/K. To determine the contribution to the TPD spectrum of thiophene desorbing from the sample holder, experiments were carried out using a blank Ni mesh. After dosing with thiophene at 190 K, no desorption features were observed in the TPD spectrum below a temperature of  $\sim 450$  K; above this temperature there was a rapid increase in the  $m/e = 84$  signal which is believed to be due to thiophene desorption from the sample holder.

The second type of experiment utilized the sample preparation and dosing procedure described above for a sulfided 17.6 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst. Following thiophene dosing at 190 K and IR spectral acquisition at 140 K, the sample was annealed at 200 K for 1 min in UHV and cooled again to 140 K, and an IR spectrum was acquired. This procedure was then repeated with the annealing temperature increased in increments of 25 K until the IR absorbances associated with adsorbed thiophene could not be detected above the background noise.

The third type of experiment involved preadsorbing CO on a sulfided 9.4 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst, followed by dosing with thiophene and IR spectral acquisition. The sample was exposed to 5.0 Torr of CO at 140 K and evacuated to UHV, and an IR spectrum was acquired. The sample was then heated to 190 K, isolated from UHV, and exposed to a saturation dose of thiophene as described above. The sample was then exposed to UHV and cooled to 140 K, and an IR spectrum was acquired.

The fourth type of experiment was carried out at temperatures of 298 K and above and consisted of acquiring IR spectra in the presence of gas-phase thiophene ( $P_{\text{Th}} = 9.5$  Torr) or a mixture of thiophene and  $\text{H}_2$  ( $P_{\text{Th}} = 9.5$  Torr,  $P_{\text{H}_2} = 490.5$  Torr). An IR spectrum of either a sample of  $\gamma$ - $\text{Al}_2\text{O}_3$  or a sulfided 9.4 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst was acquired in UHV at 298 K prior to isolating the sample from UHV and exposing it to thiophene or the thiophene/ $\text{H}_2$  mixture. Following equilibration of the sample with thiophene or the gas mixture, another IR spectrum was acquired. The sample was then heated in thiophene or the gas mixture to 693 K and held at that temperature for a time interval of 1–30 min in duration. The sample was then allowed to cool to 298 K and an IR spectrum acquired. The times listed next to the IR spectra in the figures pertaining to these experiments (Figure 7a,b) are the accumulated annealing times. Upon completion of the final anneal and IR spectral acquisition, the high-pressure cell was evacuated and the sample exposed to UHV. When the pressure had decreased to  $1.0 \times 10^{-7}$  Torr, a TPD experiment was carried out over the temperature range 300–700 K while monitoring mass-to-charge ratios of 2, 34, 41, 43, 54, and 84. An experiment in which the  $m/e$  range



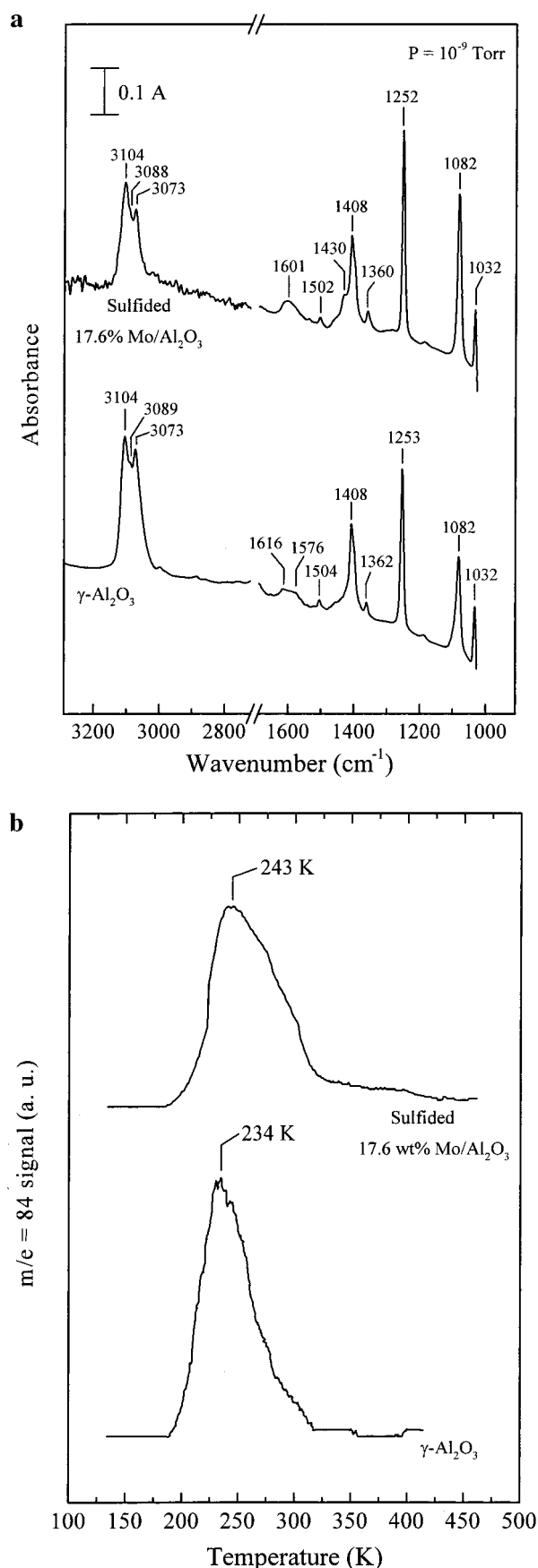
**Figure 2.** (a) Infrared and (b) TPD spectra for adsorbed CO on  $\gamma$ - $\text{Al}_2\text{O}_3$  and a sulfided 17.6 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst. The infrared spectra were acquired in UHV following dosing at 140 K.

1–100 was scanned during a TPD run revealed that no species with  $m/e > 84$  desorbed from a sulfided Mo/ $\text{Al}_2\text{O}_3$  catalyst annealed in a thiophene/ $\text{H}_2$  mixture of similar composition as given above.

All IR spectra are reproduced without any smoothing treatment and are subtraction spectra prepared by subtracting the IR spectrum acquired immediately prior to dosing with thiophene from the IR spectrum acquired after dosing or annealing. The TPD spectra presented in Figures 1 and 2 are reproduced without any smoothing treatment while those in Figure 8 were subjected to a seven-point smoothing routine. Infrared and TPD peak areas were calculated using Microcal ORIGIN software; this software program was also used for curve fitting of IR spectra as described in the Results section. The mass spectrometer was calibrated for CO and thiophene TPD measurements by simulating TPD experiments with a known amount of CO (or thiophene) gas in the high-pressure cell. In this procedure, CO (or thiophene) is leaked into the UHV chamber while collecting mass spectral data. Integration of the resulting “simulated” TPD curve yields the mass spectral response for a known amount of CO (or thiophene). These calibrations were readily reproducible and are believed to be accurate within 10%.

## Results

**Low-Temperature CO Adsorption on  $\gamma\text{-Al}_2\text{O}_3$  and on Sulfided Mo/ $\text{Al}_2\text{O}_3$  Catalysts.** Shown in Figure 2 are IR and TPD spectra acquired for samples of  $\gamma\text{-Al}_2\text{O}_3$  and a sulfided 17.6 wt % Mo/ $\text{Al}_2\text{O}_3$  catalyst dosed with a static pressure of 5.0 Torr of CO at 140 K. The IR and TPD spectra were acquired in UHV following evacuation of the gas-phase CO. The IR and TPD spectra for CO on  $\gamma\text{-Al}_2\text{O}_3$ , which was subjected to the sulfidation procedure described in the Experimental Section, are essentially identical to those observed previously in our laboratory for CO on  $\gamma\text{-Al}_2\text{O}_3$ , which was pretreated only with annealing to 600 K in UHV prior to CO adsorption.<sup>33</sup> The absorbance feature at  $2195\text{ cm}^{-1}$  is assigned to CO adsorbed on  $\text{cus Al}^{3+}$  sites of  $\gamma\text{-Al}_2\text{O}_3$ ; CO desorbs from these sites in a single TPD peak with a maximum rate of desorption at 178 K. The IR spectrum of adsorbed CO on a sulfided 17.6 wt % Mo/ $\text{Al}_2\text{O}_3$  catalyst exhibits an additional absorbance feature at  $2108\text{ cm}^{-1}$ , which has been tentatively assigned by Knözinger and co-workers<sup>37</sup> to CO adsorbed on  $\text{cus Mo}^{2+}$  sites of  $\text{MoS}_2$ -like structures. While there is agreement in the literature that sulfur vacancies located on the edge planes of  $\text{MoS}_2$  are the active sites for HDS, the oxidation state of the Mo atom exposed by formation of the vacancy remains the subject of some debate. As a result, we will refer to adsorption sites for CO (and thiophene) on sulfided Mo/ $\text{Al}_2\text{O}_3$  catalysts as “ $\text{cus Mo}^{\delta+}$  sites” throughout this article. The CO TPD spectrum for the sulfided 17.6 wt % Mo/ $\text{Al}_2\text{O}_3$  catalyst consists of a single, asymmetric peak with a maximum rate of desorption at 190 K; the trailing edge does not reach the baseline until 400 K. By comparing this TPD spectrum with that for CO on  $\gamma\text{-Al}_2\text{O}_3$ , it is clear that the trailing edge in the former is due to desorption of CO from  $\text{cus Mo}^{\delta+}$  sites of  $\text{MoS}_2$ -like structures dispersed on the alumina support. Because the CO TPD spectrum for the sulfided 17.6 wt % Mo/ $\text{Al}_2\text{O}_3$  catalyst is not resolved into separate peaks for CO desorbing from alumina and Mo sites, it is not possible to determine the CO coverage on  $\text{MoS}_2$ -like structures directly. However, the CO coverage can be estimated. From the integrated absorbance associated with CO adsorbed on  $\text{cus Al}^{3+}$  sites of the sulfided Mo/ $\text{Al}_2\text{O}_3$  catalyst, the quantity of CO adsorbed on the exposed alumina portion of the catalyst can be calculated using the extinction



**Figure 3.** (a) Infrared and (b) TPD spectra for a saturation coverage of thiophene on  $\gamma\text{-Al}_2\text{O}_3$  and a sulfided 17.6 wt % Mo/ $\text{Al}_2\text{O}_3$  catalyst. The IR spectra were acquired in UHV following dosing at 190 K and cooling to 140 K.



**TABLE 1: Vibrational Mode Assignments for Thiophene Adsorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and on a 17.6 wt % Sulfided Mo/Al<sub>2</sub>O<sub>3</sub> Catalyst (All Values in cm<sup>-1</sup>)**

C <sub>4</sub> H <sub>4</sub> S(l) (ref 39)	multilayer (ref 34)	C <sub>4</sub> H <sub>4</sub> S on $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (ref 34)	C <sub>4</sub> H <sub>4</sub> S on sulf Mo/Al <sub>2</sub> O <sub>3</sub>	assignment (ref 39)
1034	1030	1032	1032	$\delta_{\text{CH}}$ (in plane)
1080	1076	1082	1082	$\delta_{\text{CH}}$ (in plane)
1250	1250	1253	1252	$\delta_{\text{CH}}$ (in plane)
1358	1358	1362	1360	$\nu_{\text{R}}$ (ring stretch)
1406	1408	1408	1408	$\nu_{\text{CC}}$ (symmetric)
			1430	$\nu_{\text{CC}}$ (symmetric)
1504	1503	1504	1502	$\nu_{\text{CC}}$ (asymmetric)
1575	1570	1576		(combination band)
1586	1605	1616	1601	(combination band)
3072	3080	3073	3073	$\nu_{\text{CH}}$
		3089	3089	$\nu_{\text{CH}}$
3107	3100	3104	3104	$\nu_{\text{CH}}$

coefficient for CO on these sites ( $\epsilon_{\text{CO}} = (4.8 \pm 0.4) \times 10^{-18}$  cm/molecule), which was determined previously in this laboratory.<sup>33</sup> Subtracting this quantity of CO from the total amount of adsorbed CO (as determined by TPD) gives the amount of CO adsorbed on *cus* Mo<sup>δ+</sup> sites of the MoS<sub>2</sub>-like structures. This value is calculated to be CO/Mo = 0.12, which is similar to, but somewhat less than, the value determined by Maugé and Lavalley<sup>38</sup> of CO/Mo = 0.2 for a sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst (12 wt % MoO<sub>3</sub>) using a combination of IR spectroscopy and volumetric adsorption measurements. This discrepancy is not surprising given the expected higher dispersion of their catalyst ( $2.3 \times 10^{14}$  Mo atoms/cm<sup>2</sup>) when compared to the catalyst used in our work ( $7.3 \times 10^{14}$  Mo atoms/cm<sup>2</sup>).

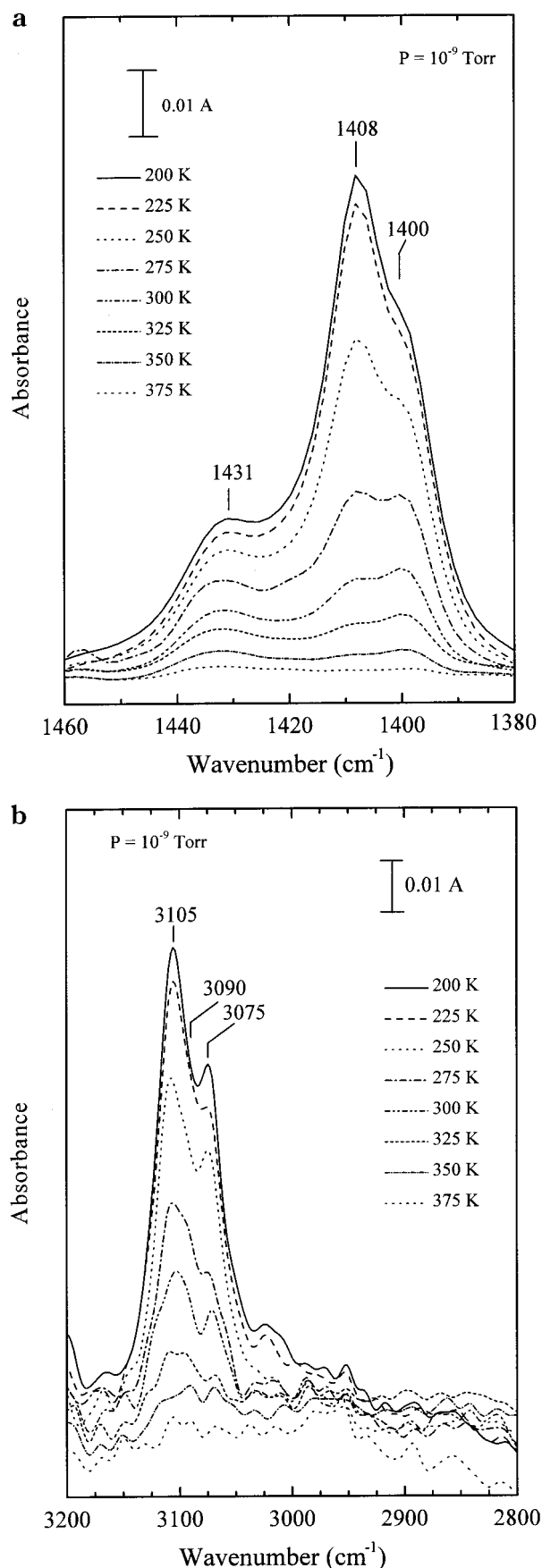
Infrared and TPD spectra of CO adsorbed on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts with 9.4 and 25.0 wt % Mo loadings were qualitatively identical to those shown here for a sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst.

**Low-Temperature Thiophene Adsorption on Sulfided Mo/Al<sub>2</sub>O<sub>3</sub> Catalysts.** Shown in Figure 3 are IR and TPD spectra for samples of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and a sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst dosed with thiophene at 190 K to give a saturation coverage. The IR spectra were acquired in UHV at a sample temperature of 140 K; the TPD spectra were acquired subsequently. The IR and TPD spectra of adsorbed thiophene on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are similar to those obtained for an alumina sample that was not subjected to the sulfidation and reduction procedures described in the Experimental Section.<sup>34</sup> The IR spectrum of adsorbed thiophene on a sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst is quite similar to the spectrum for thiophene on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Vibrational mode assignments are given in Table 1 for thiophene adsorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and on the sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. Also given in the table are peak assignments for liquid thiophene determined by Rico et al.<sup>39</sup> and for a multilayer of thiophene on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> determined previously in our laboratory.<sup>34</sup> The TPD spectrum of thiophene on the sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst consists of a single desorption peak with a maximum rate of desorption at 243 K. No other species were observed to desorb from the surface other than a small amount of hydrogen. The thiophene desorption peak for the sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst is broader and has its maximum rate of desorption at a slightly higher temperature than does the desorption peak for thiophene on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, suggesting that thiophene is somewhat more strongly bonded to the sulfided Mo catalyst.

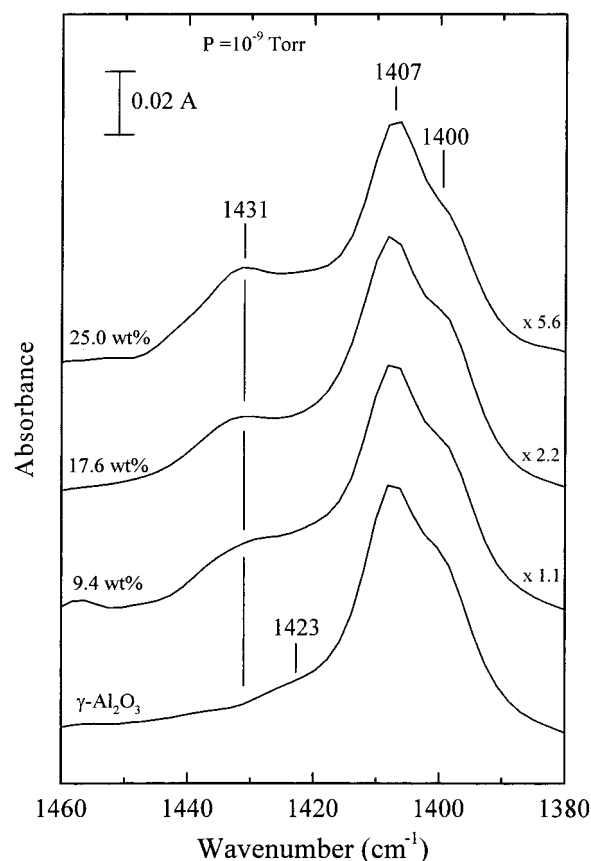
Comparison of the IR spectra of a saturation coverage of thiophene on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and on the sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst reveals one new absorbance feature on the sulfided Mo catalyst, located at 1430 cm<sup>-1</sup>. The IR spectra in Figure 4 show the changes that occur when the sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub>

catalyst dosed with a saturation coverage of thiophene is annealed to successively higher temperatures in UHV. Focusing initially on Figure 4a, three absorbance features are observed at 1400, 1408, and 1431 cm<sup>-1</sup> in the 200 K spectrum which are assigned to the  $\nu_3$  mode of thiophene.<sup>40</sup> The  $\nu_3$  mode is a ring vibration that consists primarily of the symmetric stretching of the C=C bonds of thiophene<sup>41</sup> and will hereafter be referred to as the symmetric  $\nu_{\text{CC}}$  mode of thiophene. The absorbances at 1400 and 1408 cm<sup>-1</sup> have been assigned previously to the symmetric  $\nu_{\text{CC}}$  mode of thiophene adsorbed onto the alumina support.<sup>34</sup> The absorbance feature at 1400 cm<sup>-1</sup> is associated with thiophene bonded via its sulfur atom to hydroxyl groups (C<sub>4</sub>H<sub>4</sub>S...H-O-Al) of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and the peak at 1408 cm<sup>-1</sup> is assigned to a weakly bonded, high-coverage thiophene species whose adsorption site on the alumina support is not known. As will be discussed shortly, the absorbance feature at 1431 cm<sup>-1</sup> is assigned to the symmetric  $\nu_{\text{CC}}$  mode of thiophene adsorbed on MoS<sub>2</sub>-like structures. Annealing of the sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst to successively higher temperatures leads to the preferential decrease in intensity of the absorbance feature at 1408 cm<sup>-1</sup> and the slower decrease in intensity of the  $\nu_{\text{CC}}$  absorbances at 1400 and 1431 cm<sup>-1</sup>. Reference to the IR spectrum following the 275 K anneal reveals an additional absorbance feature at  $\sim$ 1420 cm<sup>-1</sup>, which has been previously assigned to thiophene bonded via its sulfur atom to *cus* Al<sup>3+</sup> sites of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>34</sup> Following the 375 K anneal, the IR intensity has decreased essentially to the background level with the absorbance features at 1400 and 1431 cm<sup>-1</sup> the slowest to disappear. The infrared spectra in the  $\nu_{\text{CH}}$  region (Figure 4b) show similar changes upon annealing of the sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst to successively higher temperatures; absorbance features at 3075, 3090, and 3105 cm<sup>-1</sup> monotonically decrease in intensity. No new absorbance features were apparent during the annealing process, and in agreement with our TPD results, it is concluded that thiophene is reversibly adsorbed onto a sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst in UHV conditions.

To aid in the assignment of the absorbance feature at 1431 cm<sup>-1</sup>, IR spectra were acquired for a saturation coverage of thiophene on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts with a range of Mo loadings as shown in Figure 5. The absorbance feature at 1431 cm<sup>-1</sup> grows in intensity with increased Mo loading relative to the intensities of the features at 1400 and 1407 cm<sup>-1</sup> which are associated with thiophene adsorbed on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. This observation indicates that the absorbance feature at 1431 cm<sup>-1</sup> is associated with thiophene adsorbed on MoS<sub>2</sub>-like structures dispersed on the alumina support. No significant changes were observed elsewhere in the IR spectrum of adsorbed thiophene as the Mo loading was increased.



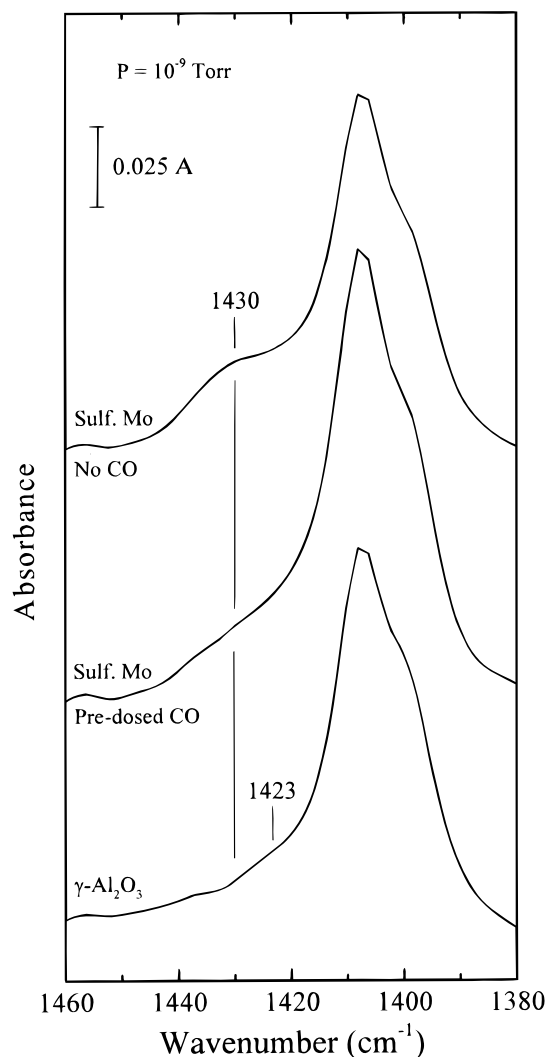
**Figure 4.** Infrared spectra in the (a)  $\nu_{CC}$  and (b)  $\nu_{CH}$  regions for thiophene adsorbed on a sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. The IR spectra were acquired at 140 K in UHV following annealing at the given temperatures for 1 min.



**Figure 5.** Infrared spectra in the  $\nu_{CC}$  region for a saturation coverage of thiophene on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts with 9.4, 17.6, and 25.0 wt % Mo loadings. The IR spectra were acquired at 140 K in UHV following dosing at 190 K.

The IR spectra presented in Figure 6 provide additional information concerning the adsorbed thiophene species associated with the absorbance feature at 1431 cm<sup>-1</sup>. In addition to IR spectra in the symmetric  $\nu_{CC}$  region of thiophene adsorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and a sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst, the IR spectrum is shown of a sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst that has been dosed with CO prior to exposure to thiophene. In this experiment, CO is adsorbed onto the catalyst at 140 K, and the sample is then heated to 190 K prior to dosing with thiophene. Although a significant amount of CO was observed to desorb when the catalyst sample was heated to 190 K, this desorbing CO originates predominantly from *cus* Al<sup>3+</sup> sites, and the majority of the *cus* Mo<sup>δ+</sup> sites should remain filled with adsorbed CO molecules. As shown in Figure 6, the presence of preadsorbed CO strongly suppresses thiophene adsorption into sites associated with the symmetric  $\nu_{CC}$  absorbance at 1431 cm<sup>-1</sup>. These results indicate, therefore, that the 1431 cm<sup>-1</sup> absorbance feature is due to thiophene adsorbed on *cus* Mo<sup>δ+</sup> sites of MoS<sub>2</sub>-like structures on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.

A direct determination of the thiophene coverage on the MoS<sub>2</sub>-like structures of the sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts investigated is not possible based upon the experiments carried out in this study. The thiophene TPD spectra for the sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts consist of a single desorption feature composed of thiophene desorbing from the alumina support and MoS<sub>2</sub>-like structures simultaneously. The saturation coverage of thiophene on the MoS<sub>2</sub>-like structures of a sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst can, however, be estimated in the following manner. Using the curve-fitting capabilities of the Microcal ORIGIN software program, the integrated absorbances of the symmetric  $\nu_{CC}$  mode for thiophene on the Mo and alumina



**Figure 6.** Infrared spectra in the  $\nu_{CC}$  region for a saturation coverage of thiophene on  $\gamma$ - $\text{Al}_2\text{O}_3$ , a sulfided 9.4 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst, and a sulfided 9.4 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst predosed with CO. The IR spectra were acquired at 140 K in UHV.

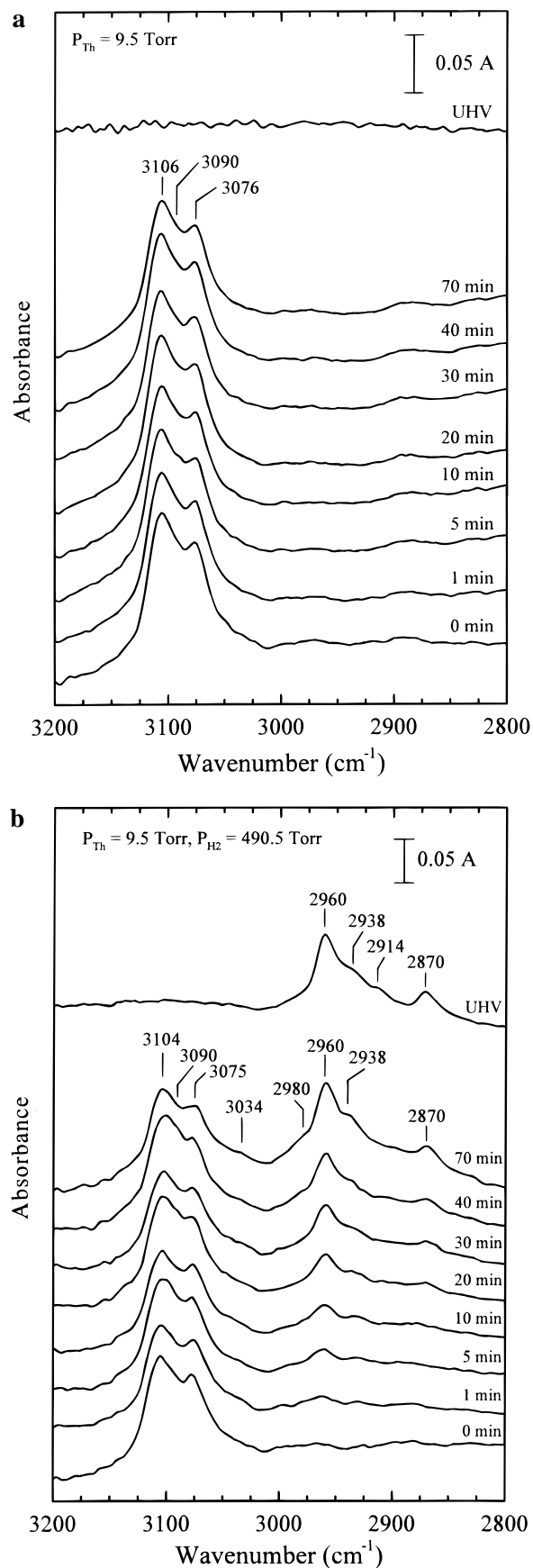
portions of a sulfided 17.6 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst were estimated. Using our previously determined value for the integrated extinction coefficient for the symmetric  $\nu_{CC}$  absorbance ( $\epsilon_{CC}$ ) of thiophene when it is adsorbed on  $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $(9.8 \pm 1.3) \times 10^{-17}$  cm<sup>2</sup>/molecule,<sup>34</sup> the concentration of thiophene molecules ( $\text{C}_4\text{H}_4\text{S}$  molecules/cm<sup>2</sup> sample disk) adsorbed on the alumina portion of the catalyst was determined via Beer's law. Knowing the cross-sectional area of the sample disk, the total amount of thiophene adsorbed on the catalyst (as determined by TPD), and the BET surface area of the catalyst, the saturation coverage of thiophene on the  $\text{MoS}_2$ -like structures of a sulfided 17.6 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst is estimated to be  $\text{C}_4\text{H}_4\text{S}/\text{Mo} = 0.074$ .

**High-Temperature Thiophene Adsorption on Sulfided  $\text{Mo}/\text{Al}_2\text{O}_3$  Catalysts.** The adsorption of thiophene on sulfided  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts was also investigated at 298 K and above. In an experiment from which the IR spectra are not presented here, a sulfided 17.6 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst was heated in the presence of 9.5 Torr of thiophene in 50 K increments over the temperature range 300–600 K. Infrared spectra were acquired while holding the sample at each temperature; the only changes observed were the gradual reduction in intensity of the absorbance features of thiophene as the sample temperature was raised

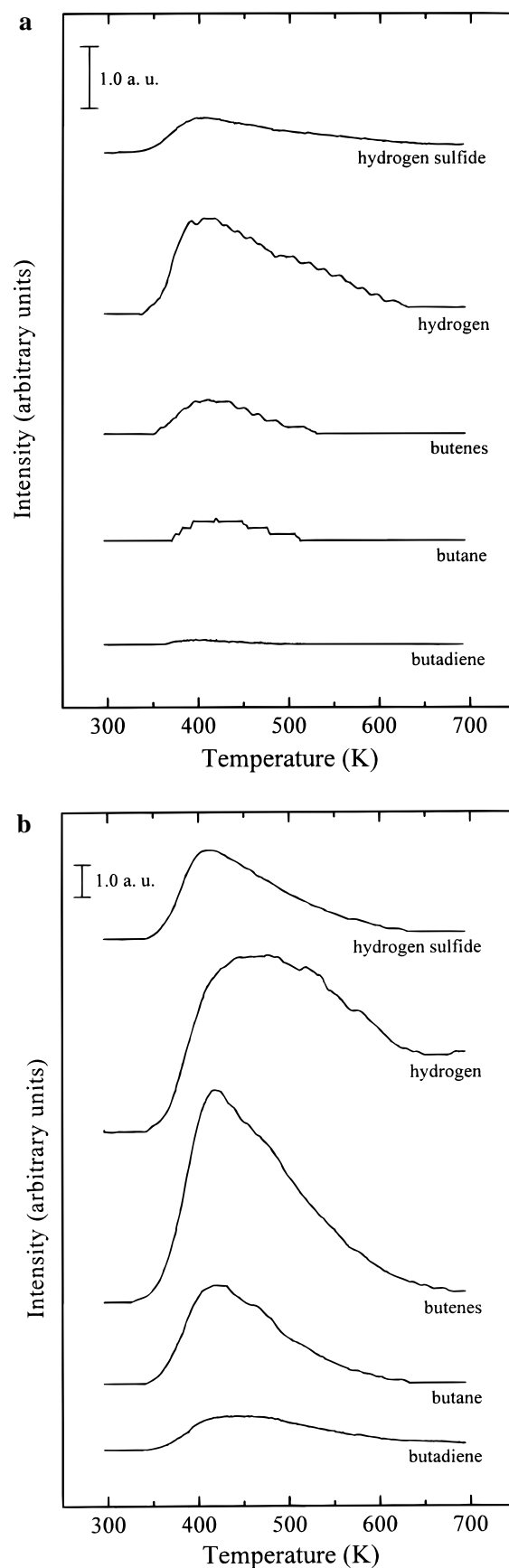
to 600 K. Within the limit of the background noise, no new absorbance features were observed to form.

The lack of reactivity of sulfided  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts toward thiophene, when heated in the vapor of this molecule alone, is demonstrated by the IR spectra in the  $\nu_{CH}$  region presented in Figure 7a. A sulfided 9.4 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst was heated to 693 K in the presence of 9.5 Torr of thiophene for the accumulated anneal times indicated on the IR spectra. Following each anneal, the catalyst sample was cooled to 298 K and an IR spectrum acquired. Comparison of the IR spectrum immediately following exposure of the catalyst to gas-phase thiophene at 298 K (labeled 0 min in Figure 7a) with those acquired after annealing shows no changes in the  $\nu_{CH}$  region. Upon completion of this annealing sequence, the gas phase was evacuated and the catalyst sample was exposed to UHV. When the pressure had decreased to  $1 \times 10^{-7}$  Torr, IR and TPD spectra were acquired. This last IR spectrum (labeled UHV in Figure 7a) shows no absorbance features attributable to adsorbed species within the limit of the background noise. Consistent with the IR spectrum, only very small desorption peaks are apparent in the TPD spectra (Figure 8a) for the expected products of thiophene HDS ( $\text{C}_4$  hydrocarbons and  $\text{H}_2\text{S}$ ); an equally small desorption peak was observed for thiophene, and this is believed to be due to desorption from the sample holder. Similar results were obtained when a sample of pure  $\gamma$ - $\text{Al}_2\text{O}_3$  was annealed to 693 K in the presence of 9.5 Torr of thiophene. No new absorbance features were observed to form, and a TPD experiment carried out following evacuation to UHV revealed only very small desorption features, similar to those in Figure 8a. It is important to note that new IR spectral features were observed to form in these experiments if the thiophene dosed was *not rigorously purified* prior to use according to the procedure described by Spies and Angelici.<sup>36</sup> This purification procedure removes trace thiol impurities present in thiophene purchased from commercial vendors. As observed previously for thiophene adsorption on  $\gamma$ - $\text{Al}_2\text{O}_3$ ,<sup>34</sup> exposure of a sulfided 9.4 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst at 298 K (or lower temperatures) to thiophene not subjected to this purification procedure resulted in the immediate formation of absorbance features in the 2850–3000 cm<sup>-1</sup> region.

Not unexpectedly, the IR spectra presented in Figure 7b show that a sulfided 9.4 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst becomes quite reactive toward thiophene when heated to 693 K in the presence of a thiophene/ $\text{H}_2$  mixture. No reactivity is observed in the identical experiment for a sample of pure  $\gamma$ - $\text{Al}_2\text{O}_3$ . Upon exposure of a sulfided  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst to a mixture of 9.5 Torr of thiophene and 490.5 Torr of  $\text{H}_2$ , the IR spectrum in the  $\nu_{CH}$  region (labeled 0 min in Figure 8a) contains absorbance features at 3075, 3090, and 3104 cm<sup>-1</sup> only, and these are assigned to thiophene adsorbed on the catalyst surface. While not shown, the IR spectrum in the  $\nu_{CC}$  region shows peaks at 1399, 1407, and 1430 cm<sup>-1</sup>, indicating that thiophene is adsorbed to sites on uncovered alumina areas as well as to sites on the  $\text{MoS}_2$ -like structures of the sulfided 9.4 wt %  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst under these conditions. Annealing of the catalyst sample at 693 K for 1 min leads to the production of new absorbance features in the  $\nu_{CH}$  region at 2938, 2960, and 3034 cm<sup>-1</sup>; further annealing produces additional absorbances at 2870 and 2980 cm<sup>-1</sup>. As will be discussed shortly, these absorbances can be assigned to the stretching vibrations of  $\text{CH}_2$  and  $\text{CH}_3$  groups of adsorbed  $\text{C}_4$  hydrocarbon species.<sup>42,43</sup> New absorbance features are observed elsewhere in the IR spectrum as well. A weak and broad absorbance feature slowly develops at approximately 2640 cm<sup>-1</sup> which is likely due to an S–H



**Figure 7.** Infrared spectra in the  $\nu_{\text{CH}}$  region for sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalysts annealed to 693 K in (a) 9.5 Torr of thiophene or (b) a thiophene/H<sub>2</sub> mixture ( $P_{\text{Th}} = 9.5$  Torr,  $P_{\text{H}_2} = 490.5$  Torr) for the accumulated times listed. The IR spectra were acquired at 298 K in the presence of the thiophene vapor or thiophene/H<sub>2</sub> mixture.



**Figure 8.** TPD spectra acquired for sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalysts after 70 min accumulated anneal time in (a) 9.5 Torr of thiophene or (b) a thiophene/H<sub>2</sub> mixture ( $P_{\text{Th}} = 9.5$  Torr,  $P_{\text{H}_2} = 490.5$  Torr). The samples were evacuated to a pressure of  $1.0 \times 10^{-7}$  Torr prior to acquiring the TPD spectra.



stretching vibration. Ratnasamy and Fripiat<sup>30</sup> observed a similar absorbance feature in their studies of H<sub>2</sub> and thiophene adsorption on unsupported MoS<sub>2</sub> and also assigned it to an S–H stretching vibration.

Following acquisition of the IR spectrum after the final anneal (70 min accumulated anneal time), the sample was exposed to UHV, and when the pressure had decreased to  $1.0 \times 10^{-7}$  Torr, an IR spectrum was acquired (labeled UHV in Figure 7b). As was the case for a sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst heated to 673 K in pure thiophene ( $P_{\text{Th}} = 9.5$  Torr), evacuation of the catalyst sample to UHV pressures results in the complete elimination of IR spectral features associated with adsorbed thiophene. As shown in Figure 7b, however, the  $\nu_{\text{CH}}$  region exhibits absorbances at 2870, 2914, 2938, and 2960 cm<sup>-1</sup> which do not decrease in intensity with further evacuation at 298 K. Absorbance features are also observed at 1076, 1134, 1213, 1260, 1271, 1312, 1330, 1443, 1460, 1611, and 2654 cm<sup>-1</sup>. The weak and very broad peak at 2654 cm<sup>-1</sup> is again assigned to an S–H vibration; this assignment is supported by the TPD spectra shown in Figure 8b which include a significant desorption peak for H<sub>2</sub>S. Of the absorbance features in the range 1050–1650 cm<sup>-1</sup>, only the absorbance at 1611 cm<sup>-1</sup> exhibits significant intensity. The absorbance features observed in the  $\nu_{\text{CH}}$  region can be assigned to the symmetric and asymmetric stretching modes of CH<sub>2</sub> and CH<sub>3</sub> groups, with the peak positions in reasonable agreement with those observed by Trombetta et al.<sup>43</sup> for butenes adsorbed on pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and those reported by Campione and Ekerdt<sup>42</sup> for butenes adsorbed on a Ni/SiO<sub>2</sub> catalyst. Similar to our IR spectrum, Trombetta et al.<sup>43</sup> also observed an absorbance feature at 1611 cm<sup>-1</sup> which they assign to the C=C stretching mode of an adsorbed allyl species with C<sub>4</sub>H<sub>7</sub> stoichiometry.

Additional information concerning the identity of the strongly adsorbed species formed by heating a sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst to 693 K in a thiophene/H<sub>2</sub> mixture can be obtained from the TPD spectra presented in Figure 8b. The TPD experiment was carried out immediately following acquisition of the UHV IR spectrum shown in Figure 7b. Substantial amounts of C<sub>4</sub> hydrocarbons as well as H<sub>2</sub> and H<sub>2</sub>S are observed to desorb from the surface of the sulfided Mo catalyst. In all cases, the desorption peaks are dramatically larger than those observed for a sample of this same catalyst that was heated in the presence of thiophene vapor alone (Figure 8a); the TPD spectra in Figure 8a have been multiplied by a factor of 2 with respect to those presented in Figure 8b. The desorption of substantial amounts of C<sub>4</sub> hydrocarbons following annealing of the sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst provides strong evidence that the absorbance features observed at 1611, 2870, 2914, 2938, and 2960 cm<sup>-1</sup> in the UHV IR spectrum are due to one or more adsorbed C<sub>4</sub> hydrocarbon species.

The TPD spectra for the sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst annealed in a thiophene/H<sub>2</sub> mixture can be compared with those presented by Jayamurthy and Vasudevan<sup>44,45</sup> for C<sub>4</sub> hydrocarbons on a sulfided 12 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. In their studies, the authors adsorbed C<sub>4</sub> hydrocarbons onto the catalyst surface at 300 K and used a mass spectrometer to monitor the desorption of species into a helium flow as the catalyst was linearly heated. Butadiene, 1-butene, and butane were observed to adsorb reversibly on the catalyst surface, desorbing at temperatures of 368, 364, and 345 K, respectively. Following annealing in a thiophene/H<sub>2</sub> mixture, we observed butadiene, butenes, and butane to desorb from the surface of a sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst with peak maxima at 440, 418, and 420 K, respectively. The higher desorption temperatures observed in

our experiment suggest that the desorption of the C<sub>4</sub> hydrocarbons is reaction limited in our case.

## Discussion

The primary objective of this study has been to identify the adsorption mode(s) of thiophene on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts and to monitor the reactivity of thiophene when adsorbed on the surfaces of these catalysts under a wide range of conditions. Before discussing our results, it is useful to first consider vibrational spectroscopic studies of adsorbed thiophene on unsupported MoS<sub>2</sub> and sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts carried out by others. Three laboratories have published IR spectra of adsorbed thiophene on unsupported MoS<sub>2</sub>. Nicholson<sup>29</sup> as well as Ratnasamy and Fripiat<sup>30</sup> observed absorbance features in the 2850–3000 cm<sup>-1</sup> spectral range immediately following thiophene adsorption on unsupported MoS<sub>2</sub> at room temperature. In both cases, the authors assigned the observed absorbance features to  $\eta^2$ - and  $\eta^4$ -coordinated thiophene on the surface of the unsupported MoS<sub>2</sub>. Annealing to higher temperatures led to an increase in intensity of the absorbance bands in the 2850–3000 cm<sup>-1</sup> region. These findings are not in agreement with those described here in which we observe no new absorbance features to form on a sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst exposed to thiophene at 298 K or annealed to 693 K in a partial pressure of 9.5 Torr of thiophene (see Figure 7a). In a previous study of thiophene adsorption on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, we observed absorbance features in the 2850–3000 cm<sup>-1</sup> range when we used thiophene (Aldrich Chemical Co., 99+% purity) that had been purified by fractional distillation over sodium prior to its adsorption on the alumina surface.<sup>34</sup> Similar results were obtained in the current study of thiophene adsorption on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. In no case do we observe absorbance features in 2850–3000 cm<sup>-1</sup> region if thiophene is subjected to the more rigorous purification scheme described by Angelici and co-workers.<sup>36</sup> While we cannot rule out the possibility of unsupported MoS<sub>2</sub> and sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts having different reactivity toward thiophene, we believe that the absorbance features observed in the 2850–3000 cm<sup>-1</sup> range by Nicholson<sup>29</sup> and by Ratnasamy and Fripiat<sup>30</sup> are due to thiol impurities in their thiophene.

In their studies, Diemann et al.<sup>31</sup> exposed samples of unsupported MoS<sub>2</sub> and of a sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst to a flow of either argon or H<sub>2</sub> containing thiophene and then acquired an infrared emission (IRE) spectrum of the unsupported sample and Raman and inelastic electron tunneling (IET) spectra of the supported samples. Exposure of the samples to thiophene (in Ar or H<sub>2</sub>), subsequent purging in argon, and acquisition of the vibrational spectra were all carried out at a sample temperature of 670 K. No peaks were observed in the spectral range investigated (200–1500 cm<sup>-1</sup>) for the MoS<sub>2</sub> and sulfided Mo/Al<sub>2</sub>O<sub>3</sub> samples exposed to thiophene in an argon flow while a number of peaks were observed for the samples exposed to thiophene in a hydrogen flow. Despite the fact that some of the observed peak positions were consistent with those of thiophene, no absorbance feature was observed that could be assigned to the symmetric  $\nu_{\text{CC}}$  mode of thiophene. In the IET spectrum of the sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst exposed to the thiophene/H<sub>2</sub> flow at 670 K, the authors assign a vibrational feature at 300 cm<sup>-1</sup> to the Mo–S stretching vibration and tentatively conclude that thiophene is  $\eta^1(\text{S})$ -coordinated to the catalyst surface. However, the absence of a symmetric  $\nu_{\text{CC}}$  absorbance in their spectra is puzzling, and our studies suggest that thiophene is quite reactive when a sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst is exposed to a thiophene/H<sub>2</sub> mixture at 693 K, just

**TABLE 2: Comparison of Bond Lengths (in Å) in Free and Coordinated Thiophene**

compound	C(2)–S	C(5)–S	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	ref
free thiophene (T)	1.714 ± 0.001	1.714 ± 0.001	1.370 ± 0.002	1.424 ± 0.002	1.370 ± 0.002	55
$\eta^1(\text{S})$ -Bound						
(PPh <sub>3</sub> ) <sub>2</sub> Ru(C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> C <sub>4</sub> H <sub>3</sub> S) <sup>+</sup>	1.754 ± 0.006	1.734 ± 0.006	1.344 ± 0.008	1.409 ± 0.008	1.339 ± 0.008	56
Cp(CO)(PPh <sub>3</sub> )Ru(2-MeT) <sup>+</sup>	1.753 ± 0.005	1.756 ± 0.005	1.350 ± 0.007	1.417 ± 0.008	1.329 ± 0.008	57
$\eta^4$ -Bound						
Cp*Ir(2,5-Me <sub>2</sub> T)	1.76 ± 0.02	1.79 ± 0.02	1.43 ± 0.02	1.39 ± 0.02	1.46 ± 0.02	58
$\eta^5$ -Bound						
(CO) <sub>3</sub> Cr(2,5-Me <sub>2</sub> T)	1.754 ± 0.002	1.758 ± 0.002	1.383 ± 0.003	1.422 ± 0.003	1.385 ± 0.003	59
(C <sub>5</sub> H <sub>12</sub> )Rh(2,5-Me <sub>2</sub> T)	1.764 ± 0.006	1.743 ± 0.006	1.409 ± 0.008	1.377 ± 0.008	1.390 ± 0.007	60
(PPh <sub>3</sub> ) <sub>2</sub> Rh(T)	1.73 ± 0.01	1.73 ± 0.01	1.40 ± 0.02	1.38 ± 0.02	1.43 ± 0.02	61

above the temperature of 670 K employed by Diemann et al. Also, our TPD studies in UHV conditions indicate that thiophene desorption from a sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst is complete by 400 K while TPD studies in flowing He and H<sub>2</sub> by Jayamurthy and Vasudevan<sup>44,45</sup> indicate that thiophene desorption from a sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst is complete by 600 K. It is likely, therefore, that the predominant surface species under the conditions utilized by Diemann et al.<sup>31</sup> are strongly adsorbed reaction products with the coverage of thiophene likely to be very low.

Finally, Mitchell et al.<sup>32</sup> utilized inelastic neutron scattering (INS) to investigate the vibrational spectrum of adsorbed thiophene on a sulfided Mo/Al<sub>2</sub>O<sub>3</sub> (14 wt % MoO<sub>3</sub>) catalyst. The catalyst was exposed to thiophene at room temperature prior to spectral acquisition at 20 K. While all vibrational modes are neutron-active, INS is most sensitive to motions involving hydrogen, and the reported INS spectra (400–2000 cm<sup>-1</sup>) show only vibrational modes associated with in-plane and out-of-plane bending motions of the ring hydrogen atoms. For thiophene adsorbed on a freshly sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst, small decreases are observed in the intensities of the out-of-plane C–H modes compared with those of liquid thiophene, while the intensities of the in-plane C–H modes are essentially unchanged. On the basis of these observations, the authors conclude that thiophene is  $\eta^5$ -coordinated to the catalyst surface. For thiophene adsorbed on a sulfided, then freshly reduced Mo/Al<sub>2</sub>O<sub>3</sub> catalyst, the authors conclude that both  $\eta^1(\text{S})$ - and  $\eta^5$ -coordinated thiophene species are present on the catalyst surface as both the in-plane and out-of-plane C–H modes are diminished in intensity. The changes in intensity of the peaks in the INS spectra are small, and the fact that only spectral features associated with C–H bending motions were observed makes it difficult to interpret the INS spectra.

To our knowledge, the results presented here permit the first definitive assignment of the adsorption mode of thiophene on a sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. As described in the Results section, an absorbance feature at 1431 cm<sup>-1</sup> in the IR spectrum of thiophene adsorbed on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts can be assigned to the symmetric  $\nu_{\text{CC}}$  mode of thiophene adsorbed on MoS<sub>2</sub>-like structures. The peak position of this  $\nu_{\text{CC}}$  mode is shifted 25 cm<sup>-1</sup> higher than is observed for liquid thiophene (see Table 1), and this shift is useful in determining the adsorption mode of thiophene on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. It is well-known that the vibrational frequencies of ring stretching modes of heterocyclic aromatic molecules are sensitive to their bonding environment on a catalyst surface. Spectral shifts of the 8a and 19b ring modes when pyridine is adsorbed on metal oxide surfaces, for example, are used to identify the types of adsorption sites on these materials.<sup>46</sup> The peak position of the 8a mode of pyridine, which involves the symmetric stretching of the  $\alpha$ -CC bonds<sup>47</sup> (similar to the symmetric  $\nu_{\text{CC}}$  mode of thiophene), shifts 43 cm<sup>-1</sup> higher than its value in liquid

pyridine when pyridine is coordinated via its nitrogen atom to *cis* Al<sup>3+</sup> sites of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>48</sup> Studies in our laboratory have shown that the symmetric  $\nu_{\text{CC}}$  mode of thiophene shifts from 1406 cm<sup>-1</sup> in liquid thiophene to 1424 cm<sup>-1</sup> when thiophene coordinates via its sulfur atom to *cis* Al<sup>3+</sup> sites of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>34</sup> The fact that the peak position of this same  $\nu_{\text{CC}}$  mode shifts to 1431 cm<sup>-1</sup> when thiophene is adsorbed onto MoS<sub>2</sub>-like structures of sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts provides the first evidence that thiophene is coordinated via its sulfur atom ( $\eta^1(\text{S})$ ) to *cis* Mo<sup>δ+</sup> sites on the catalyst surface.

A search of the literature revealed two thiophene-containing organometallic complexes that have been characterized by vibrational spectroscopic methods. Infrared and Raman spectra have been obtained for (CO)<sub>3</sub>Cr( $\eta^5$ -T) (T = C<sub>4</sub>H<sub>4</sub>S)<sup>49,50</sup> while IR spectra have been reported for [Cp(CO)<sub>2</sub>Fe( $\eta^1(\text{S})$ -3-MeT)]-BF<sub>4</sub> (MeT = C<sub>5</sub>H<sub>6</sub>S).<sup>51</sup> Lokshin et al.<sup>49</sup> assigned the vibrational modes of thiophene in (CO)<sub>3</sub>Cr( $\eta^5$ -T) and noted that the greatest shifts occurred for the ring stretching and out-of-plane C–H bending modes. The symmetric  $\nu_{\text{CC}}$  mode is observed at 1391 cm<sup>-1</sup>, or 15 cm<sup>-1</sup> lower than is observed for liquid thiophene. This shift is in the opposite direction than we observed for adsorbed thiophene on a sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst; in this case the  $\nu_{\text{CC}}$  mode is shifted 25 cm<sup>-1</sup> higher to 1431 cm<sup>-1</sup>. Less information can be obtained from the IR spectra of [Cp(CO)<sub>2</sub>-Fe( $\eta^1(\text{S})$ -3-MeT)]BF<sub>4</sub> reported by Butler et al.<sup>51</sup> as vibrational modes of the Cp ligand overlap with those of 3-methylthiophene in many cases. An absorbance feature at 1383 cm<sup>-1</sup> can be attributed to a CH<sub>3</sub> bending mode of 3-methylthiophene,<sup>52</sup> while an absorbance feature at 1423 cm<sup>-1</sup> can be assigned to the asymmetric  $\nu_{\text{CC}}$  mode of the Cp ligand.<sup>53</sup> No absorbance feature was observed between the peaks at 1383 and 1423 cm<sup>-1</sup>, indicating that the symmetric  $\nu_{\text{CC}}$  absorbance of the thiophene ligand is shifted from that of liquid thiophene, but no further information on its position can be extracted from the IR spectrum of [Cp(CO)<sub>2</sub>Fe( $\eta^1(\text{S})$ -3-MeT)]BF<sub>4</sub>.

Additional information to aid in the interpretation of the IR spectrum of adsorbed thiophene on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts can be obtained from a surface-enhanced Raman spectroscopy (SERS) study of 3-chlorothiophene adsorbed in silver sol. Mukherjee and Misra<sup>54</sup> noted a shift of the  $\nu_{\text{CC}}$  absorbance from 1408 cm<sup>-1</sup> for the pure liquid to 1420 cm<sup>-1</sup> when 3-chlorothiophene is adsorbed on the silver sol. The SERS spectrum also shows an absorbance at 163 cm<sup>-1</sup> which the authors assign to the Ag–S stretching mode, indicating that 3-chlorothiophene is bonded to the silver surface through the sulfur atom. These results provide strong evidence that coordination of thiophenes to a surface via the ring sulfur atom causes a shift of the symmetric  $\nu_{\text{CC}}$  absorbance to higher wavenumbers.

Further evidence that thiophene is  $\eta^1(\text{S})$ -bonded to sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts can be drawn from X-ray structural data for thiophene-containing organometallic complexes which are summarized in Table 2.<sup>55–61</sup> For the few cases in which

sufficiently accurate structural data have been obtained, important differences are observed in the C=C bond lengths as a function of the thiophene adsorption mode. When thiophenes are  $\eta^1(\text{S})$ -bonded to a metal center, the C=C bond lengths (C(2)–C(3) and C(4)–C(5)) become significantly shorter than those in free thiophene while the opposite is observed for thiophene which is  $\eta^4$ - or  $\eta^5$ -bonded to a metal center. These structural data clearly indicate that coordination of thiophene to a metal center via its sulfur atom ( $\eta^1(\text{S})$ ) causes a strengthening of the C=C bonds while a weakening of these same bonds is observed for  $\pi$ -bonded thiophenes ( $\eta^4$ - and  $\eta^5$ -coordination). On the basis of the bond lengths determined from the X-ray structural data, therefore, we would predict that the symmetric  $\nu_{\text{CC}}$  mode should be shifted to *higher* wavenumbers when thiophene is  $\eta^1(\text{S})$ -bonded to a metal center (or surface) and should be shifted to *lower* wavenumbers when thiophene is  $\pi$ -bonded to a metal center (or surface). To our knowledge, accurate X-ray structural data have not been reported in the literature for an organometallic complex containing an  $\eta^2$ -bonded thiophene.

The vibrational and structural data presented above for organometallic complexes containing thiophenes, as well as the SERS spectra of 3-chlorothiophene adsorbed in a silver sol, permit a conclusive interpretation of the IR spectra of adsorbed thiophene on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. The shift of the symmetric  $\nu_{\text{CC}}$  mode of thiophene from 1406 cm<sup>-1</sup> for liquid thiophene to 1431 cm<sup>-1</sup> for adsorbed thiophene indicates that thiophene is  $\eta^1(\text{S})$ -bonded to MoS<sub>2</sub>-like structures dispersed on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. Furthermore, it can be concluded that thiophene adsorbs on *cus* Mo<sup>δ+</sup> sites located on edge planes of MoS<sub>2</sub>-like structures as preadsorption of CO on these sites effectively blocks thiophene chemisorption onto the alumina-supported MoS<sub>2</sub>-like structures (see Figure 6). As indicated by the TPD spectrum presented in Figure 3b, thiophene is only weakly chemisorbed on *cus* Mo<sup>δ+</sup> sites of sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, desorbing in a single peak with a maximum rate of desorption at 243 K. Excluding small desorption peaks for H<sub>2</sub> and H<sub>2</sub>S, no other desorption features were detected, indicating that no thiophene decomposition occurs on the catalyst surface under UHV conditions. This conclusion is supported by the IR spectra shown in Figure 4 in which only the gradual reduction of IR intensity in the  $\nu_{\text{CC}}$  and  $\nu_{\text{CH}}$  regions is observed as a sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst with a saturation coverage of thiophene is annealed to increasing temperatures in UHV.

The observation that  $\eta^1(\text{S})$ -bonded thiophene is only weakly chemisorbed to sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts is consistent with both organometallic and theoretical studies of thiophene bonding, and the results of these studies can be used to gain additional insight into thiophene adsorption on sulfided Mo catalysts. As discussed by Angelici,<sup>4</sup> thiophene is a weakly coordinating ligand when  $\eta^1(\text{S})$ -bonded to a metal center, and as a result, thiophene is often displaced by other ligands. In those cases in which X-ray crystal structures have been obtained, the thiophene ring is tilted with respect to the metal–sulfur bond (see Figure 1), and this has been interpreted in terms of approximate sp<sup>3</sup> hybridization of the sulfur atom.<sup>4</sup> In Cp(CO)(PPh<sub>3</sub>)Ru(2-MeT)<sup>+</sup> and (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>S)Ru(PPh<sub>3</sub>)<sub>2</sub>, for which accurate X-ray structural data have been obtained,<sup>56,57</sup> the C–S bond lengths are approximately 0.04 Å longer than in free thiophene (see Table 2). Angelici suggests that C–S bond lengthening and pyramidalization of the sulfur atom are due to a decrease in the aromaticity of the thiophene ring. Jin and Xue<sup>62</sup> arrived at a similar conclusion to explain the shift of the symmetric  $\nu_{\text{CC}}$  absorbance in the Raman spectra of thiophene

in solvated Lewis acids. As the strength of the Lewis acid was increased, the symmetric  $\nu_{\text{CC}}$  mode of thiophene shifted from 1407 cm<sup>-1</sup> for pure thiophene to 1410.5 cm<sup>-1</sup> for thiophene in an BF<sub>3</sub>–ethyl ether solution. The authors concluded that the interaction of thiophene with Lewis acids decreases the aromaticity of the thiophene ring and leads to increased localization of electrons on the C=C bonds. The fact that the C=C bonds are significantly shorter in Cp(CO)(PPh<sub>3</sub>)Ru(2-MeT)<sup>+</sup> and (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>S)Ru(PPh<sub>3</sub>)<sub>2</sub> than in free thiophene is consistent with this interpretation as well. Focusing again on adsorbed thiophene on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, we conclude that  $\eta^1(\text{S})$ -bonded thiophene adopts a bonding geometry in which the thiophene ring is most likely tilted toward the catalyst surface. Coordination of thiophene to a *cus* Mo<sup>δ+</sup> site decreases the aromatic character of the thiophene ring, resulting in increased localization of electron density in the C=C bonds and weakening of the C–S bonds.

A number of researchers have carried out theoretical investigations of thiophene bonding in organometallic complexes,<sup>63,64</sup> metal sulfide clusters,<sup>6,65</sup> and thiophene adsorption on slabs of MoS<sub>2</sub>.<sup>5</sup> Consistent with our experimental studies, these theoretical investigations predict that  $\eta^1(\text{S})$ -coordinated thiophene should be relatively weakly bonded in an organometallic complex or to a vacancy in a metal sulfide. In most cases,  $\pi$ -bonded thiophene ( $\eta^4$  or  $\eta^5$ ) is predicted to be more stable than thiophene bonded via its sulfur atom ( $\eta^1(\text{S})$ ),<sup>6,65</sup> although both experimental and theoretical studies suggest that the thiophene adsorption mode is sensitive to the thiophene coverage,<sup>3</sup> the presence of coadsorbed hydrogen,<sup>65</sup> and the degree of coordinate unsaturation of the adsorption site.<sup>5</sup>

In addition to predicting that  $\eta^1(\text{S})$ -coordinated thiophene should be weakly adsorbed to catalyst surfaces, theoretical studies suggest that adsorption in this geometry should produce only minor perturbations of the bonding within the thiophene molecule. Two groups have carried out theoretical investigations of thiophene bonding in organometallic complexes containing  $\eta^1(\text{S})$ -coordinated thiophene. Employing Fenske–Hall molecular orbital (MO) calculations, Harris<sup>63</sup> described the bonding of thiophene in [Cp(CO)<sub>2</sub>Fe( $\eta^1(\text{S})$ -T)]<sup>+</sup> as consisting of donation of electrons from the 2b<sub>1</sub> and 1a<sub>1</sub> orbitals of thiophene to the metal center with negligible back-donation of electrons into the unoccupied 3b<sub>1</sub> orbital of thiophene. Since the 2b<sub>1</sub> and 1a<sub>1</sub> orbitals are primarily sulfur lone pair orbitals, depopulation of these orbitals was found to have minimal effects on the thiophene ring. More recently, Sargent and Titus<sup>64</sup> have utilized density functional theory (DFT) to examine the bonding of thiophene  $\eta^1(\text{S})$ -coordinated to Cp\*Rh(PMe<sub>3</sub>). The authors describe the bonding of thiophene in this complex to consist principally of donation of electron density (0.26 e<sup>-</sup>) from a sulfur lone pair fragment molecular orbital (FMO) to the metal center but also note that approximately 0.15 electron is transferred back to the unoccupied 2b<sub>2</sub> orbital of thiophene. Interestingly, the thiophene FMO from which 0.26 electron is transferred to the rhodium is a linear combination of the 2a<sup>1</sup> (1a<sup>1</sup> in Harris' study) and 2b<sup>1</sup> orbitals on thiophene and has slight antibonding C(2)–C(3) character. This theoretical observation suggests that donation of electrons from this FMO to the metal center should slightly increase the C=C bond strength, which would explain the shorter C=C bond lengths in  $\eta^1(\text{S})$  thiophene complexes and the higher peak position of the symmetric  $\nu_{\text{CC}}$  absorbance when thiophene is adsorbed on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. It should be noted that recent theoretical calculations carried out by Rodriguez<sup>6</sup> predict a slightly shorter C=C bond length when thiophene is  $\eta^1(\text{S})$ -



bonded to an a-top site of a MoS<sub>2</sub> cluster. This is in contrast to thiophene which is  $\eta^5$ -bonded to the same cluster for which the C=C bond lengths are substantially longer than in free thiophene.

In addition to identifying the adsorption mode of thiophene on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, the results presented here provide new insight into the surface chemistry involved in thiophene HDS over sulfided Mo catalysts. As mentioned in the Introduction, it has not been possible to directly observe intermediate species in the C–S insertion reaction in organo-metallic complexes although indirect evidence points to  $\eta^1$ (S)-coordinated thiophene being the immediate precursor.<sup>9</sup> Our studies of thiophene adsorption and reaction provide no evidence for formation of a C–S insertion product on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. Under UHV conditions, thiophene is reversibly adsorbed on a sulfided 17.6 wt % sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst, with desorption complete by ~400 K as indicated by the IR and TPD spectra presented in Figures 3 and 4. Even under conditions of higher pressure ( $P_{\text{Th}} = 9.5$  Torr) and temperature ( $T = 693$  K), no reactivity is observed for thiophene on a sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst when the catalyst is annealed for a total of 70 min in the presence of the gas-phase thiophene (see Figures 7a and 8a).

We have observed thiophene to become reactive on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts only when the catalysts are annealed to high temperatures (i.e., 693 K) in the presence of a thiophene/hydrogen mixture. These results are in contrast to those published previously by others<sup>29,30</sup> which showed thiophene to be reactive when adsorbed alone on unsupported MoS<sub>2</sub> and sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts at considerably lower temperatures. The IR spectra presented in Figure 7b clearly show that one or more hydrogenated species, exhibiting IR absorbance features in the region 2870–2960 cm<sup>-1</sup>, are produced on a sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst when it is annealed to 693 K in a mixture of 9.5 Torr of thiophene and 490.5 Torr of H<sub>2</sub>. Evacuation of the sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst following 70 min of accumulated annealing results in desorption of chemisorbed thiophene, but the hydrogenated species produced during the annealing process remain adsorbed on the catalyst surface as shown in the UHV IR spectrum (see Figure 7b). The fact that absorbance features associated with thiophene are removed upon evacuation at 298 K indicates that more strongly adsorbed forms of thiophene are not formed during the annealing process. Temperature-programmed desorption spectra acquired after the UHV IR spectrum (see Figure 8b) reveal desorption peaks for C<sub>4</sub> hydrocarbons, H<sub>2</sub>, and H<sub>2</sub>S with maximum rates of desorption at 440, 420, and 418 K for butadiene, butenes, and butane, respectively. Jayamurthy and Vasudevan<sup>45,44</sup> carried out a TPD study of C<sub>4</sub> hydrocarbons on a sulfided 12 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst in which the different species were adsorbed and desorbed into a helium flow passing over the catalyst. Following their adsorption at 300 K, butadiene, 1-butene, and butane were observed to desorb with maximum rates of desorption at 368, 364, and 345 K, respectively. These desorption temperatures are substantially lower than those measured by us for TPD following annealing in the thiophene/H<sub>2</sub> mixture. Jayamurthy and Vasudevan also carried out TPD measurements in flowing hydrogen. Following adsorption of 1-butene, TPD in flowing H<sub>2</sub> resulted in butene desorption peaks at 363 and 426 K, as well as a butane desorption peak at 528 K. The only hydrocarbon observed to desorb into flowing H<sub>2</sub> following butadiene adsorption was butane at a temperature of 368 K. The butene desorption peak observed in our TPD occurs at a similar temperature as the second butene desorption peak

observed by Jayamurthy and Vasudevan following 1-butene adsorption, while the butane desorption peak measured in our studies occurs at a temperature between those measured by these authors following butene and butadiene adsorption.

While it is difficult to directly compare the TPD spectra obtained by Jayamurthy and Vasudevan<sup>44,45</sup> with ours because of the different conditions employed, it is possible to draw the following conclusions. The desorption of C<sub>4</sub> hydrocarbons from a sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst annealed in a thiophene/H<sub>2</sub> mixture is reaction limited, suggesting the presence of one or more strongly adsorbed intermediate species on the catalyst surface with C<sub>4</sub>H<sub>y</sub> stoichiometry. As discussed in the Results section, the peak positions of the most intense absorbance features in the IR spectrum acquired following evacuation of the thiophene/H<sub>2</sub> mixture are in reasonably good agreement with those obtained by Trombetta et al.<sup>43</sup> following adsorption of *cis*- and *trans*-2-butene on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. These authors assign the absorbance features observed in their IR spectra to a  $\sigma$ -bonded allyl species of C<sub>4</sub>H<sub>7</sub> stoichiometry. It is conceivable that this is the same species we observe to form on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts during annealing in a thiophene/H<sub>2</sub> mixture, although it is presumably bonded to *cus* Mo <sup>$\delta^+$</sup>  sites on our catalyst. An adsorbed C<sub>4</sub>H<sub>7</sub> species could be expected to undergo dehydrogenation to give butadiene or hydrogenation to give the more predominant butene and butane products during TPD.

One final point we would like to address concerns the relationship between CO and thiophene adsorption sites on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. Studies in our laboratory<sup>66</sup> and by Bachelier et al.<sup>67</sup> have shown that the thiophene HDS activity of sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts correlates linearly with the CO adsorption capacities of the catalysts, clearly suggesting that the adsorption sites are the same for these two molecules. To our knowledge, the results presented here provide the first direct evidence to support this conclusion. As shown in Figure 6, preadsorption of CO on a sulfided 9.4 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst blocks thiophene adsorption into sites associated with the absorbance feature at 1431 cm<sup>-1</sup>. This observation allows us to conclude that CO and thiophene compete for *cus* Mo <sup>$\delta^+$</sup>  adsorption sites on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. The fact that there is a correlation between CO adsorption capacity and HDS activity provides further evidence that *cus* Mo <sup>$\delta^+$</sup>  sites are not only the sites on which thiophene adsorbs but also the sites on which HDS occurs. As described in the Results section, the experiments carried out in this study allow us to estimate the saturation coverages of CO and thiophene on a sulfided 17.6 wt % Mo/Al<sub>2</sub>O<sub>3</sub> catalyst to be CO/Mo = 0.12 and C<sub>4</sub>H<sub>4</sub>S/Mo = 0.074. It is not particularly surprising that the saturation coverage of thiophene is lower than that of CO as a sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst likely has adsorption sites that are accessible to CO but not to the bulkier thiophene molecule. This discrepancy in the saturation coverages of CO and thiophene also underscores the fact that while normalizing thiophene HDS activity using the CO adsorption capacity provides a useful means of comparing catalyst activities for a series of catalysts, there is likely to be a fairly large error in the absolute value of a turnover frequency determined in this manner.

## Conclusion

Infrared spectroscopic investigation of adsorbed thiophene on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts at low temperatures has allowed us to determine that thiophene is  $\eta^1$ (S)-bonded to *cus* Mo <sup>$\delta^+$</sup>  sites on MoS<sub>2</sub>-like structures. Thiophene is weakly chemisorbed on to these sites, and no reactivity is observed either under UHV conditions or in a partial pressure of 9.5 Torr of thiophene at



temperatures up to 693 K. As monitored by IR spectroscopy, thiophene becomes reactive on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts when it is heated in a thiophene/H<sub>2</sub> mixture at 693 K. A definitive assignment of the IR spectral features of strongly adsorbed species produced during annealing in the thiophene/H<sub>2</sub> mixture cannot be made, but the peak positions are similar to those observed by Trombetta et al.<sup>43</sup> following adsorption of butenes on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and which were assigned to an adsorbed C<sub>4</sub>H<sub>7</sub> species. Temperature-programmed desorption spectra are consistent with the presence of such an adsorbed intermediate as reaction-limited desorption of butadiene, butenes, and butane (as well as H<sub>2</sub>S and H<sub>2</sub>) from the surface is observed. Further studies are necessary in order to fully understand the reaction pathway for thiophene HDS on sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts.

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