JOURNAL OF CATALYSIS **178,** 226–233 (1998)
ARTICLE NO. CA982162

Mechanisms of Thiophene Hydrodesulfurization on Model Molybdenum Catalysts

David L. Sullivan[1] and John G. Ekerdt[2]

Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712

Received January 28, 1998; revised May 14, 1998; accepted May 18, 1998

Hydrodesulfurization (HDS) activities and selectivities were measured for thiophene, tetrahydrothiophene (THT), and 1-butanethiol on silica-supported molybdenum catalysts at a pressure of 1 atm and temperatures ranging from 530 to 795 K. The model catalysts, which were previously characterized, feature isolated molybdenum atoms in the +2, +4, and +6 oxidation states and molybdenum dimers with each molybdenum atom in the +4 oxidation state. Silica-supported MoS_2 was used for reference. Activities for thiophene and THT HDS correlate with oxidation state. Mo(II) is most active among dispersed catalysts. 1-Butanethiol activities were much larger than thiophene or THT activities and were roughly equal on all dispersed catalysts. Apparent activation energies of 43.4 and 48.5 kJ/mol were determined for thiophene HDS on Mo(II) and MoS_2/SiO_2, respectively. Apparent activation energies of 132 and 174 kJ/mol were determined for THT HDS on Mo(II) and MoS_2/SiO_2, respectively. Dihydrothiophene, THT and 1-butanethiol were formed in thiophene HDS over Mo(II) and MoS_2/SiO_2. The major products of thiophene and THT HDS were 1-butene, 2-butene, and *n*-butene. Butadiene, *i*-butane, *i*-butene, methane, ethane, ethene, propane, and propene were formed in small amounts. Butadiene is thought to be the initial product of thiophene and THT desulfurization and undergoes subsequent hydrogenation and isomerization to yield the observed products. A common mechanism for HDS of thiophene and THT with 2,5-DHT as an intermediate is discussed.

INTRODUCTION

Removal of sulfur from petroleum feedstocks is accomplished by hydrodesulfurization (HDS) in which the petroleum is treated with hydrogen over a $CoMoS/Al_2O_3$ catalyst at temperatures from 573 to 723 K and pressures from 35 to 100 atm. Several reviews of catalyst structure and properties have been published (1–5). The industrial catalyst consists of molybdenum oxide supported on γ-alumina, which is promoted with cobalt or nickel. The supported metal oxides are presulfided before use. Molybdenum is reduced during sulfidation from the +6 oxidation state of MoO_3 to the +4 oxidation state of MoS_2. Formation of MoS_2 has been shown by many techniques including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), extended X-ray absorption fine structure spectroscopy, and Raman spectroscopy. MoS_2 forms crystallites with a layered structure under these conditions (6).

The active sites on MoS_2/Al_2O_3 are thought to be molybdenum atoms on the perimeter of the MoS_2 crystallites that have sulfur vacancies and are in an oxidation state lower than +4 (7, 8). We have used isolated Mo(II), isolated Mo(IV), and isolated Mo(VI) to study oxidation state effects in thiophene HDS (9). The perimeter of MoS_2 crystallites contains two distinct environments (8, 10). The $(10\bar{1}0)$ face contains sulfur atoms that are bound to only one molybdenum atom. The $(\bar{1}010)$ face contains sulfur atoms that are bound to two molybdenum atoms. Active sites created by removal of these sulfur atoms will present different environments for thiophene adsorption. We have used isolated Mo(IV), dimeric Mo(IV), and MoS_2/SiO_2 to study structural effects in thiophene HDS (9). XPS and XRD were used to show that the Mo(II) and Mo(IV) did not change oxidation states or become sulfided during thiophene HDS. Thiophene HDS activity was shown to correlate with the oxidation state, Mo(II) being the most active. MoS_2/SiO_2 was much more active than Mo(II) but had the same activation energy as Mo(II). The product distributions of thiophene HDS on Mo(II), isolated Mo(IV), dimeric Mo(IV), and MoS_2/SiO_2 were similar, indicating that the catalyst oxidation state and structure do not significantly affect the reaction mechanism. The activity of isolated Mo(IV) for thiophene HDS shows that a site containing multiple metal atoms is not needed for reaction and the equivalent activities of isolated Mo(IV) and dimeric Mo(IV) show that multiple metal atoms do not enhance activity.

η^1 and η^5 binding of thiophene have been observed in organometallic complexes (11) and on single crystal metal surfaces (2). Binding of thiophene to an active site is thought to weaken the C-S bonds, thereby promoting reaction. In organometallic complexes, the C-S bonds of

---

[1] Current address: SABIC Americas, 16200-A Park Row, Houston, Texas 77084.

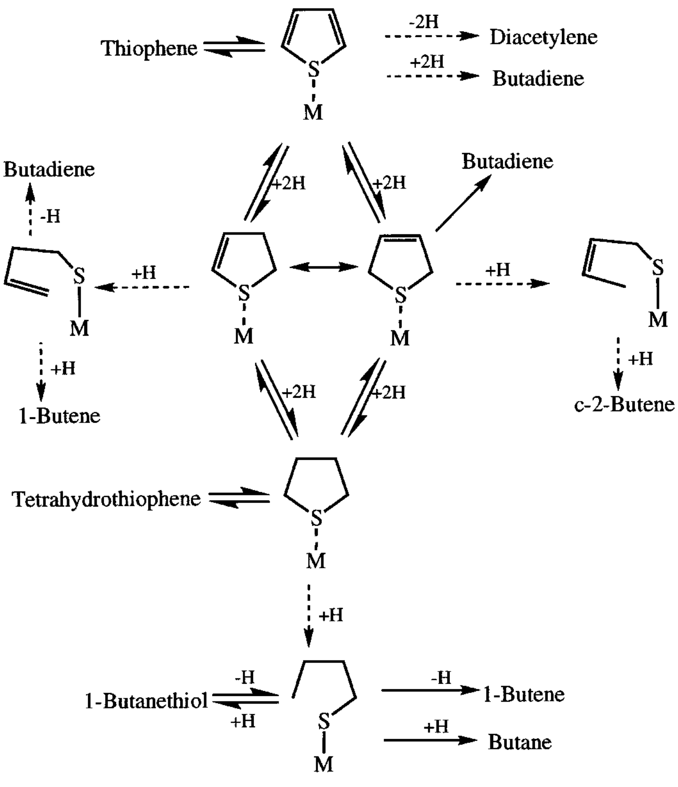
[2] Corresponding author. E-mail: ekerdt@che.utexas.edu.

0021-9517/98 $25.00

η^5-thiophene ligands are weaker than those of η^1-thiophene ligands and η^5-thiophene ligands are more reactive than η^1-thiophene ligands. η^5-thiophene is a six-electron donor, requiring a site with three vacancies. η^1-thiophene is a two-electron donor, requiring only a singly unsaturated site. The activity of isolated Mo(IV) (9), which is only capable of accepting two electrons (1 coordination vacancy), indicates that HDS can be initiated by η^1-adsorption of thiophene. Sulfhydryl (-SH) groups have been shown to be weak Brønsted acids and are thought to be a source of hydrogen for the hydrogenation and hydrogenolysis reactions (12, 13). Metal hydryl (-MH) groups have been detected by neutron scattering of unsupported RuS_2 and may also be involved in hydrogenation and hydrogenolysis (10, 14). The activity of isolated Mo(IV), which is not capable of binding both thiophene and hydrogen, indicates that metal hydryl groups are not required for HDS. For the dispersed catalysts, which lack sulfhydryl groups, hydrogen for hydrogenation and hydrogenolysis probably comes from hydroxyl groups on the silica surface.

Thiophene is typically used as a model reactant because it is representative of the aromatic sulfur-containing compounds that are difficult to desulfurize. Mechanisms for thiophene HDS have been proposed, based on results from small scale reactors (15–21), single crystal metal surfaces (22–25), organometallic complexes (11, 26), Chevrel phases (27), and supported metal clusters (28). These mechanisms are summarized in Scheme 1. Kolboe studied HDS of thiophene, tetrahydrothiophene (THT), and 1-butanethiol over unsupported MoS_2 and $CoMoS/Al_2O_3$ (17). He proposed that thiophene and THT are not hydrogenated and do not share a common intermediate and that HDS occurs by transfer of the β-hydrogen atoms to the sulfur atom with concurrent C-S bond cleavage. Thiophene would form diacetylene and THT would form butadiene, which would be hydrogenated to butene and butane (17, 29 30). Lipsch and Schuit proposed that the C-S bonds of thiophene undergo hydrogenolysis to form butadiene, which is hydrogenated to butene and butane (16). However, direct cleavage of the strong aromatic C-S bonds would be difficult (26, 30, 31). In the hydrogenation mechanism, hydrogenation of one or both C=C bonds occurs before C-S bond scission (11, 22, 32). Removal of the aromatic stability of thiophene by hydrogenation would make C-S bond scission much easier. Hydrogenolysis of the C-S bonds of dihydrothiophene (DHT) may compete with hydrogenation of the C=C bond (32). Similar product distributions have been observed in the HDS of thiophene, DHT, and THT, suggesting that they are desulfurized by the same mechanism (18, 29).

Thiophene, THT, and 2,5-DHT adsorbed on Mo(110) react by independent mechanisms (23–25). Thiophene adsorbed on Mo(110) decomposes to surface carbon, sulfur, and hydrogen with no hydrocarbon products (23, 24). 2,5-DHT adsorbed on Mo(110) eliminates butadiene in about 60% yield; the rest decomposes to surface carbon, sulfur, and hydrogen (25). Formation of butadiene from 2,5-DHT has also been observed on Re/Al_2O_3 and Mo/Al_2O_3 catalysts and in organometallic complexes (21, 26). THT on Mo(110) reacts through a 1-butanethiolate intermediate to form 1-butene and butane (23). Only 25% of the THT produced hydrocarbons; the rest decomposed to surface carbon, sulfur, and hydrogen.



SCHEME 1

DHT, THT, and 1-butanethiolate are proposed intermediates in thiophene HDS (18–26, 29, 33–35). This paper examines the degree of thiophene hydrogenation during HDS to gain a better understanding of the reaction mechanism. The activities and selectivities of model molybdenum catalysts and silica-supported MoS_2 for thiophene, THT and 1-butanethiol HDS are presented. 2,5-DHT is shown to be the key intermediate in thiophene and THT HDS.

METHODS

All samples were supported on Cab-O-Sil HS 5 silica (Cabot, 325 m^2/g) in a quartz U-tube that permitted sample preparation in an inert atmosphere and flow-through reactions. Mo(II), isolated Mo(IV), dimeric Mo(IV), Mo(VI), and MoS_2/SiO_2 were prepared as before (9). For MoS_2/SiO_2, XRD indicates that crystallites are formed with an average size of 48 Å–134 Å, and approximately 10% of the molybdenum atoms on the perimeter. Atomic absorption spectroscopy was used to determine the molybdenum content of the catalysts. Weight loadings varied from 0.5% to 5.0% molybdenum. The number of moles of molybdenum used to calculate turnover frequencies (TOFs) (mol reacted/mol Mo-sec) and turnover numbers (TONs) (total mol reacted/mol Mo) for Mo(II), dimeric Mo(IV), and Mo(VI) catalysts is the number of moles of molybdenum present on the catalyst. TOFs and TONs for isolated Mo(IV) were based on the number of moles of Mo(IV) formed by photoreduction. The activity of isolated Mo(IV) was corrected for the activity of the unreduced Mo(VI). TOFs and TONs for MoS_2/SiO_2 were based on the amount of molybdenum on the perimeter.

XRD and XPS were performed as before (9, 36). *Ex situ* XRD was performed following HDS to determine whether MoS_2 crystallites formed during HDS. The oxidation states of representative samples of Mo(II), dimeric Mo(IV), and Mo(VI) were determined before and after HDS by *in situ* XPS. Mo(II) shows Mo $3d_{3/2}$ and $3d_{5/2}$ binding energies of 231.6 ± 0.1 and 228.5 ± 0.1 eV, respectively, and dimeric Mo(IV) shows Mo $3d_{3/2}$ and $3d_{5/2}$ binding energies of 235.0 ± 0.2 and 231.8 ± 0.1 eV, respectively (9). X-ray photoelectron spectra were collected with a physical electronics system. Chamber pressure during measurement was on the order of 10^{-9} Torr. Samples were transferred from the reaction U-tube to the XPS chamber under an inert atmosphere by use of a dry box and an airtight sample transfer case. The oxidation state of isolated Mo(IV) catalysts was not verified by XPS due to the presence of unreduced Mo(VI). Isolated Mo(IV) catalysts were prepared by photoreduction of isolated Mo(VI) samples in CO, which is known to produce isolated Mo(IV) (9, 36, 37).

Thiophene (Janssen, 99+%), THT (Aldrich, 99%), and 1-butanethiol (Janssen, 98+%) were purified by several freeze/pump/thaw cycles before use. The major impurities in the thiophene were methanethiol (0.1%) and 1-butanethiol (0.04%). The thiophene did not contain detectable amounts of THT or DHT. Thiophene was fed to the catalysts by hydrogen flow at 4 to 8 ml/min through a saturator containing liquid thiophene at 295 K and 1 atm, resulting in 8.7% thiophene in hydrogen. Conversions for thiophene HDS were between 1% and 7%. The major impurity in the THT was 1-butanethiol (0.21%). The THT did not contain detectable amounts of thiophene or DHT. THT was fed to the catalysts by hydrogen flow at 8 to 18 ml/min through a saturator containing liquid THT at 295 K and 1 atm, resulting in 1.9% THT in hydrogen. Conversions for THT HDS were between 1% and 6%. The only detectable impurity in the 1-butanethiol was thiophene (0.50%). 1-Butanethiol was fed to the catalysts by hydrogen flow at 8 to 20 ml/min through a saturator containing liquid 1-butanethiol at 1 atm and 273 K or 295 K, resulting in 1.5% and 4.5% 1-butanethiol in hydrogen, respectively. Conversions for 1-butanethiol HDS were between 4% and 24%.

Hydrogenation and isomerization of 1-butene and butadiene were studied to determine whether these reactions might occur after desulfurization of thiophene, THT, and 1-butanethiol. 1-Butene in helium (5400 ppm) and butadiene in helium (3900 ppm) were mixed with hydrogen to give flow rates of about 20 ml/min and concentrations of about 500 ppm, to approximate the flow rates and concentrations present during the HDS experiments. Hydrogenation and isomerization of 1-butene and butadiene with Mo(II), dimeric Mo(IV), and MoS_2/SiO_2 catalysts were studied at a pressure of 1 atm and a temperature of 530 K. Reaction of butadiene with simultaneous thiophene HDS was studied to determine whether hydrogenation of butadiene was possible in the presence of thiophene. Five ml/min butadiene in helium was mixed with 18 ml/min hydrogen and passed through the thiophene saturator. Reaction of this mixture with MoS_2/SiO_2 catalysts was studied at a pressure of 1 atm and temperatures of 530 and 660 K.

2,5-DHT was synthesized by reaction of 1,4-dichloro-2-butene with sodium sulfide (38). *cis*-1,4-Dichloro-2-butene (Aldrich, 95%) in methanol (Aldrich, 99.9+%) and sodium sulfide (EM Science, 98%) in methanol were added dropwise to a stirred solution of methanol and methylsulfoxide (Aldrich, 99.9%). The mixture was added to distilled water and extractions with pentane (EM Science, 98%) were performed. The combined extracts were washed with distilled water and dried with anhydrous $MgSO_4$ (EM Science). Since the 2,5-DHT was only used to measure its gas chromatograph retention time, the 2,5-DHT was not separated from the pentane. The successful synthesis of 2,5-DHT was verified by ^1H NMR (δ of 3.67 and 5.81 ppm) (39). The NMR indicated a small amount of decomposition of 2,5-DHT to 2,3-DHT (δ of 2.74, 3.21, 5.59, and 6.14 ppm) (40).

The effluent from the reaction U-tube was sampled on-line with a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector. A 1-ml sample from an automatic gas sampling valve was injected onto a 50 m, 0.53 mm PLOT Al_2O_3/KCl column (Chrompak). The detector was calibrated with a 1010 ppm CH_4/1010 ppm C_3H_8/He mixture (Matheson, certified). The relative sensitivity of the FID was corrected by using effective carbon numbers (41). Effective carbon numbers of 3.0, 2.9, 3.0, and 3.5 were used for thiophene, DHT, THT, and 1-butanethiol, respectively. A mixture of C_1-C_4 hydrocarbons in helium (in-house) was used to calibrate retention times. Retention times for thiophene, DHTs, THT, and 1-butanethiol were individually determined by injecting the genuine compounds.

RESULTS

Ex situ XRD and *in situ* XPS were used to determine whether the catalysts changed oxidation state or were

TABLE 1

Turnover Frequencies for Thiophene, THT, and 1-Butanethiol HDS at 530 K

Catalyst	Thiophene (1/s × 10^6)	THT (1/s × 10^6)	1-Butanethiol (1/s × 10^6)
Mo(II)	56	14	460
Isolated Mo(IV)	29	4.1	480
Dimeric Mo(IV)[a]	27	5.6	360
Mo(VI)	2.0	0.22	280
MoS_2/SiO_2	240	460	3170

[a] Turnover frequency is per molybdenum atom. One dimer is counted as two sites.

sulfided during HDS. Previous work has shown that Mo(II), isolated Mo(IV), and dimeric Mo(IV) do not change oxidation state or become sulfided during thiophene HDS at temperatures less than 800 K (9). Mo(VI) formed MoS_2 crystallites in thiophene HDS at temperatures above 650 K (9). XRD and XPS results (not shown) of catalysts used for THT and 1-butanethiol HDS are similar to those for thiophene HDS. Electron binding energies and oxidation states of all catalysts measured before HDS agree with literature values (42, 43) and have not changed following THT and 1-butanethiol HDS. Mo(II), isolated Mo(IV), dimeric Mo(IV), and Mo(VI) do not change oxidation state or become sulfided during THT or 1-butanethiol HDS at temperatures less than 800 K.

Table 1 shows TOFs for thiophene, THT, and 1-butanethiol HDS at 530 K. Figure 1 shows TOFs for thiophene and THT HDS on Mo(II) and MoS_2/SiO_2 at temperatures from 530 to 795 K. Apparent activation energies of 48.5 and 43.4 kJ/mol were determined for thiophene HDS on MoS_2/SiO_2 and Mo(II), respectively. Apparent activation energies of 174 and 132 kJ/mol were determined for THT HDS on MoS_2/SiO_2 and Mo(II), respectively. THT has higher activity than thiophene at temperatures above 515 and 580 K on MoS_2/SiO_2 and Mo(II), respectively. For all catalysts, 1-butanethiol HDS is much faster than thiophene and THT HDS.

C_4H_x products of thiophene, THT, and 1-butanethiol HDS on MoS_2/SiO_2, Mo(II), isolated Mo(IV), and dimeric Mo(IV) at 530 K are shown in Figs. 2, 3, 4, and 5, respectively. The temperature of 530 K was chosen for the majority of experiments to try to minimize secondary hydrogenation and isomerization reactions. Product distributions at higher temperatures are similar to those at 530 K but show small decreases in the amounts of butadiene and DHT and small increases in the amounts of butenes and *n*-butane. 1-Butanethiol HDS produced only *n*-butane, 1-butene, and 2-butene. The major products of thiophene and THT HDS are 1-butene, *n*-butane, and 2-butene. Butadiene, light products (methane, ethane, ethene, propane, and propene) and cracking products (*i*-butene and *i*-butane) were detected in thiophene and THT HDS. The C_4H_x products of thiophene and THT HDS are similar. Table 2 shows the product distributions, including sulfur-containing compounds, for thiophene and THT HDS on Mo(II) and MoS_2/SiO_2 at 530 K and low conversion (<2%). Thiophene HDS on Mo(II) and MoS_2/SiO_2 produces moderate amounts of THT and light products and small amounts of 1-butanethiol, 2,5-DHT, and 2,3-DHT. 1-Butanethiol was detected in the products of THT HDS on Mo(II) and MoS_2/SiO_2; however, it was present in amounts lower than the impurity level of the THT feed. 2,5-DHT and

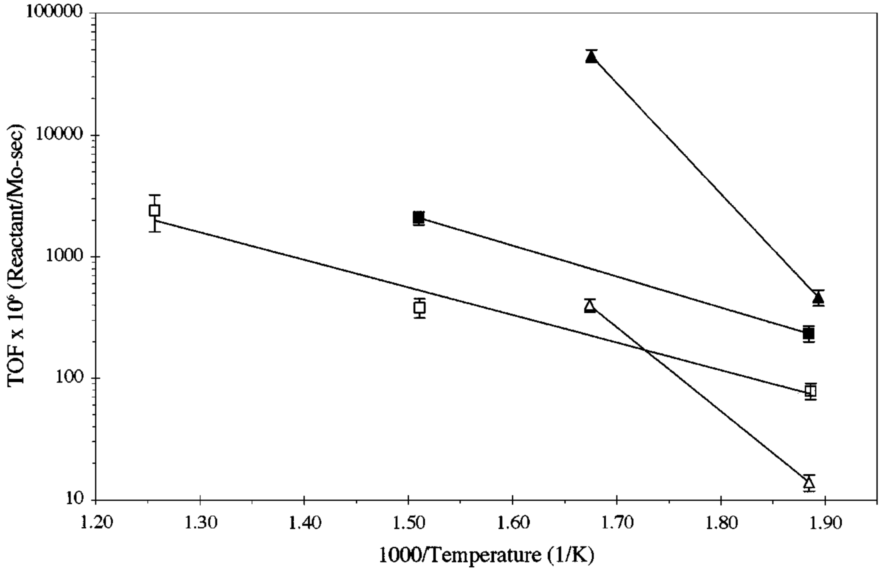


FIG. 1. HDS activities for thiophene on Mo(II) (□), THT on Mo(II) (△), thiophene on MoS_2/SiO_2 (■), and THT on MoS_2/SiO_2 (▲).

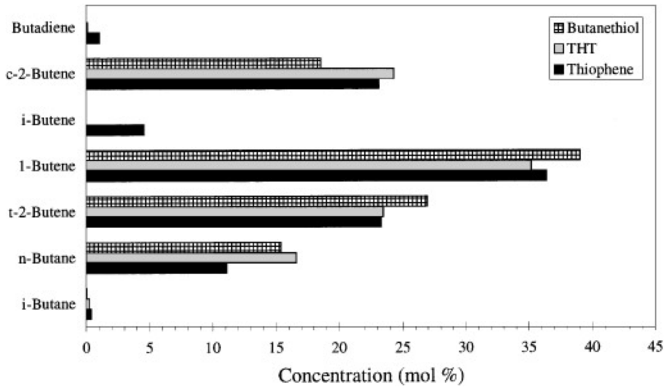


FIG. 2. C_4H_x products of thiophene, THT, and 1-butanethiol HDS on MoS_2/SiO_2 at 530 K.

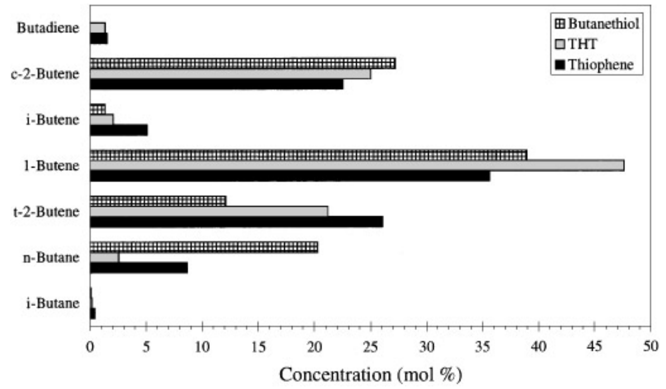


FIG. 4. C_4H_x products of thiophene, THT, and 1-butanethiol HDS on isolated Mo(IV) at 530 K.

2,3-DHT were not detected in THT HDS on MoS_2/SiO_2. Thiophene was not detected in THT HDS on Mo(II) or MoS_2/SiO_2.

Product distributions for the reaction of 1-butene in hydrogen and butadiene in hydrogen with Mo(II), dimeric Mo(IV), and MoS_2/SiO_2 catalysts are shown in Tables 3 and 4, respectively. Hydrogenation of butadiene is nearly complete. Hydrogenation and isomerization of 1-butene are rapid. The product distribution of thiophene HDS with added butadiene for MoS_2/SiO_2 at 660 K is shown in Table 5. Also shown in Table 5 are the product distribution for thiophene HDS on MoS_2/SiO_2 at 660 K and the calculated product distribution for thiophene HDS with added butadiene if no butadiene reacted. Similar results were obtained for thiophene HDS with butadiene on MoS_2/SiO_2 at 530 K. The products of thiophene HDS with butadiene are similar to those for thiophene HDS only.

DISCUSSION

HDS of thiophene and THT may occur through many possible intermediates: 2,5-DHT to form butadiene; 2,5-DHT and 2-butene-1-thiolate to form *cis*-2-butene; 2,3-DHT and 3-butene-1-thiolate to form 1-butene and butadiene; or 1-butanethiolate to form 1-butene and *n*-butane (Scheme 1). Formation of THT and 1-butanethiol in thiophene HDS on Mo(II) and MoS_2/SiO_2 (Table 2) agrees with thiophene HDS on MoS_2, MoS_2/C, and MoS_2/Al_2O_3 (19, 20, 26) and could suggest that thiophene HDS proceeds through THT and 1-butanethiolate intermediates. However, the product distributions observed for thiophene and THT HDS are not similar to those for 1-butanethiol HDS. Butadiene, DHTs, and light products are formed in thiophene and THT HDS, but not in 1-butanethiol HDS. Furthermore, THT cannot be a major intermediate in thiophene HDS since the activation energy for THT HDS is higher than that for thiophene HDS. Activation energies for thiophene and THT HDS on Mo(II) and MoS_2/SiO_2 are comparable to those with MoS_2/Al_2O_3 and $CoMoS/Al_2O_3$ catalysts (20, 26, 29, 34, 35). If THT was a major intermediate in thiophene HDS, the activation energy for thiophene HDS would equal or exceed that for THT HDS. The large amount of THT formed in thiophene HDS indicates that complete hydrogenation of the thiophene ring is

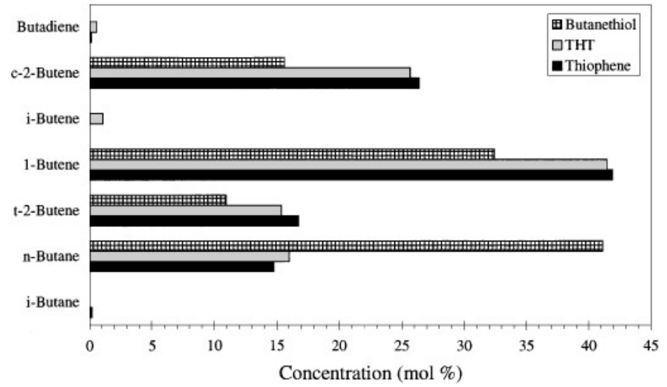


FIG. 3. C_4H_x products of thiophene, THT, and 1-butanethiol HDS on Mo(II) at 530 K.

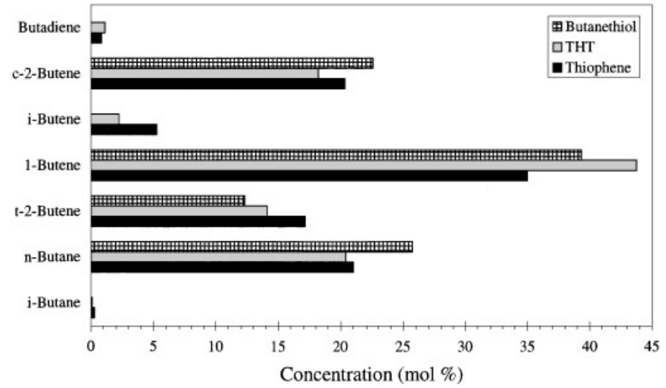


FIG. 5. C_4H_x products of thiophene, THT, and 1-butanethiol HDS on dimeric Mo(IV) at 530 K.

TABLE 2

Product Distributions (mol%) for Thiophene and THT HDS on Mo(II) and MoS_2/SiO_2 at 530 K

Products	Thiophene reactant		Tetrahydrothiophene reactant	
	Mo(II)	MoS_2/SiO_2	Mo(II)	MoS_2/SiO_2
2,3-Dihydrothiophene	0.04	0.22	0.23	0^a
2,5-Dihydrothiophene	0.29	0.28	0.40	0^a
Tetrahydrothiophene	25	23	—	—
1-Butanethiol	1.2	0.13	0^b	0^b
Butadiene	0.21	0.77	0.31	0.13
Butene	59	61	78	81
Butane	8.1	8.0	15	16
C_1-C_3	6.6	6.4	5.6	2.0

[a] Not detected. Detection limit is approximately 0.02%.

[b] Present but at a concentration lower than the impurity level of the feed.

energetically feasible. Formation of 1-butanethiol indicates that hydrogenolysis of THT is possible, but the activation energies and the small amount formed indicate that it is not a major path for HDS. Evidently, the activation energy for hydrogenolysis of THT is larger than that for dehydrogenation of THT.

The similarity of product distributions for thiophene and THT HDS suggests that they react by a common path. Based on our results and the literature (11, 21, 25, 26), 2,5-DHT is probably the common intermediate in thiophene and THT HDS. Formation of DHTs in thiophene and THT HDS on Mo(II) and MoS_2/SiO_2 is shown by us, in agreement with the formation of DHTs in thiophene HDS on MoS_2/C and CoMoS/C (20). DHTs have not been observed in thiophene or THT HDS on MoS_2/Al_2O_3 or $CoMoS/Al_2O_3$, but they must be formed in the interconversion of thiophene and THT (18, 26). The absence of DHTs in thiophene and THT HDS on MoS_2/Al_2O_3 and $CoMoS/Al_2O_3$ is probably due to their high activities at the temperatures typically used (20, 26). Our experiments are at lower temperatures than others and allow us to observe DHTs in thiophene and THT HDS.

It has been shown that 1-butene is present in thiophene and THT HDS in amounts in excess of equilibrium (9, 18, 24, 27). The presence of *trans*-2-butene indicates that isomerization is occurring since *trans*-2-butene cannot be a direct product of thiophene, DHT, THT, or 1-butanethiol HDS. We have shown that hydrogenation of butadiene is rapid and gives product distributions similar to those for thiophene and THT HDS. We have also shown that butadiene hydrogenation is rapid in the presence of thiophene. These results suggest that butadiene is the initial product of thiophene and THT HDS and that it undergoes subsequent hydrogenation and isomerization reactions. Butadiene is probably formed by elimination of sulfur from 2,5-DHT (11, 21, 25, 26). We suggest that the major path for thiophene HDS is hydrogenation to 2,5-DHT and elimination of sulfur to produce butadiene. The major path for THT HDS is dehydrogenation to 2,5-DHT and elimination of sulfur to produce butadiene. The observed mixture of C_4H_x products is formed by subsequent hydrogenation and isomerization reactions. We can infer that the activation energy for THT reaction to 1-butanethiolate is significantly higher than that for THT dehydrogenation to DHT and butadiene elimination.

The *cis*-2-butene to *trans*-2-butene ratio of roughly 1 to 1 indicates that isomerization occurs by a carbenium ion intermediate on a Brønsted acid site. Sulfhydryl groups on MoS_2 (12) and hydroxyl groups on SiO_2 (44) are weak Brønsted acids and may be sites for 1-butene isomerization on MoS_2/SiO_2 and the dispersed catalysts, respectively. The slight excess of *cis*-2-butene suggests that a small amount is a primary desulfurization product. 2,5-DHT may undergo hydrogenolysis to 2-butene-1-thiolate to yield *cis*-2-butene. Similarly, a small amount of 2,3-DHT may undergo hydrogenolysis to 3-butene-1-thiolate to yield 1-butene and butadiene. The difference in the amount of *cis*-2-butene and *trans*-2-butene in thiophene and THT HDS is small, so most of the 2-butene is produced by isomerization of 1-butene. Therefore, the butenethiolates are only minor intermediates in thiophene and THT HDS.

Unlike thiophene and THT, 1-butanethiol does not show a strong correlation between activity and the oxidation state. 1-Butanethiol is much more reactive than THT. The only products of 1-butanethiol HDS are 1-butene, *cis*-2-butene, *trans*-2-butene, and *n*-butane. Thiophene, THT, DHTs, butadiene, light products, and cracking products are

TABLE 3

Product Distributions (mol%) for Hydrogenation of 1-Butene at 530 K

Catalyst	Products (mol%)						
	C_1-C_3	*i*-Butane	*N*-Butane	*1*-Butene	*c*-2-Butene	*t*-2-Butene	*i*-Butene
Mo(II)	0.87	0	58	16	12	10	0
Dimeric Mo(IV)	0.02	0	11	42	30	17	0
MoS_2/SiO_2	0.55	0.21	28	39	20	12	0

TABLE 4

Product Distributions (mol%) for Hydrogenation of Butadiene at 530 K

Catalyst	Products (mol%)			
	C_1-C_3	Butane	Butene	Butadiene
Mo(II)	0.93	44	53	2.4
Dimeric Mo(IV)	1.4	51	48	0.02
MoS_2/SiO_2	0.62	18	72	9.7

not formed in 1-butanethiol HDS. These results agree with those on CoMoS/Al_2O_3 (23) and suggest that 1-butanethiol HDS proceeds by a different mechanism than thiophene and THT HDS. 1-Butene and *n*-butane are probably the initial products with 2-butene formed by isomerization of 1-butene (23).

Isolated Mo(II), which is tetrahedrally coordinated with two Mo-O bonds and two vacancies, is an 8-electron center. Isolated Mo(IV), which has four Mo-O bonds and one vacancy, is a 10-electron center. Thiophene HDS activities per coordination vacancy are similar for the Mo(II) and Mo(IV) catalysts (Table 1), suggesting that oxidation state may not be the dominant factor in determining the activity of a site. Rather, the number of coordination vacancies may control the activity of a site. This would imply that each atom of the Mo(IV) dimers is an active site and that the two vacancies of Mo(II) act as two active sites. Unfortunately lower oxidation state and increased coordination vacancy are coupled and cannot be studied independently. The THT HDS activities per vacancy for the Mo(II) and Mo(IV) catalysts are close but not similar, which could suggest that the identical thiophene HDS activities per vacancy are merely coincidental. We believe that the higher activity of Mo(II), compared to Mo(IV), is due to a stronger interaction of thiophene with more reduced molybdenum atoms, thereby increasing the rate of hydrogenation of thiophene. It appears that the oxidation state does not affect the reaction mechanism, merely the rate of reaction.

In summary, the activation energies and product distributions for thiophene and THT HDS suggest that the major path for HDS is the elimination of sulfur from 2,5-DHT to produce butadiene. 1-Butene, 2-butene, and *n*-butane are formed by hydrogenation and isomerization. Some reaction of thiophene and THT through thiolate intermediates does occur, but these pathways are minor.

TABLE 5

Product Distributions (mol%) for Thiophene and Butadiene Reaction on MoS_2/SiO_2 at 660 K

	Products (mol%)			
	C_1-C_3	Butane	Butene	Butadiene
Thiophene HDS	3.3	14.2	81.9	0.6
Thiophene HDS with butadiene reaction	2.3	14.3	80.9	1.5
Thiophene HDS with butadiene (as diluent)	2.1	9.2	54.2	35.8

ACKNOWLEDGMENTS

This work was supported by grants from the U.S. Department of Energy, Office of Basic Energy Sciences (Grant DE-FG03-95ER14570) and the Exxon Foundation. We gratefully acknowledge the assistance of Sandra Whaley and Dr. Deborah Hess of the Department of Chemistry and Biochemistry for assistance with the XPS.

REFERENCES

1. Grange, P., *Catal. Rev. Sci. Eng.* **21**, 135 (1980).
2. Prins, R., de Beer, V. H. J., and Somorjai, G. A., *Catal. Rev. Sci. Eng.* **31**, 1 (1989).
3. Ratnasamy, P., and Sivasanker, S., *Catal. Rev. Sci. Eng.* **22**, 401 (1980).
4. Topsøe, H., and Clausen, B. S., *Catal. Rev. Sci. Eng.* **26**, 395 (1984).
5. Chianelli, R. R., *Catal. Rev. Sci. Eng.* **26**, 361 (1984).
6. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **139**, 631 (1993).
7. Daage, M., and Chianelli, R. R., *J. Catal.* **149**, 414 (1994).
8. Drew, M. G. B., Mitchell, P. C. H., and Kasztelan, S., *J. Chem. Soc. Farad. Trans.* **86**, 697 (1990).
9. Sullivan, D. L., and Ekerdt, J. G., *J. Catal.* **172**, 64 (1997).
10. Kasztelan, S., *Langmuir* **6**, 590 (1990).
11. Angelici, R. J., *Bull. Soc. Chim. Belg.* **104**, 265 (1995).
12. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **119**, 252 (1989).
13. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **139**, 641 (1993).
14. Jobic, H., Clugnet, G., Lacroix, M., Yuan, S., Mirodatos, C., and Breysse, M., *J. Am. Chem. Soc.* **115**, 3654 (1993).
15. Mitchell, P. C. H., *Catalysis (London)* **4**, 175 (1981).
16. Lipsch, J. M. J. G., and Schuit, G. C. A., *J. Catal.* **15**, 179 (1969).
17. Kolboe, S., *Can. J. Chem.* **47**, 352 (1969).
18. Desikan, P., and Amberg, C. H., *Can. J. Chem.* **42**, 843 (1964).
19. Kieran, P., and Kemball, C., *J. Catal.* **4**, 394 (1965).
20. Hensen, E. J. M., Vissenberg, M. J., de Beer, V. H. J., van Veen, J. A. R., and van Santen, R. A., *J. Catal.* **163**, 429 (1996).
21. Sauer, N. N., and Angelici, *Inorg. Chem.* **26**, 2160 (1987).
22. Weigand, B. C., and Friend, C. M., *Chem. Rev.* **92**, 491 (1992).
23. Roberts, J. T., and Friend, C. M., *J. Am. Chem. Soc.* **108**, 7204 (1986).
24. Zaera, F., Kollin, E. B., and Gland, J. L. *Surf. Sci.* **184**, 75 (1987).
25. Liu, A. C., and Friend, C. M., *J. Am. Chem. Soc.* **113**, 820 (1991).
26. Markel, E. J., Schrader, G. L., Sauer, N. N., and Angelici, R. J., *J. Catal.* **116**, 11 (1989).
27. Ekman, M. E., Anderegg, J. W., and Schrader, G. L., *J. Catal.* **117**, 246 (1989).
28. Neurock, M., and van Santen, R. A., *J. Am. Chem. Soc.* **116**, 4427 (1994).
29. Hargreaves, A. E., and Ross, J. R. H., *J. Catal.* **56**, 363 (1979).
30. Kraus, J., and Zdrazil, M., *React. Kinet. Catal. Lett.* **6**, 475 (1977).
31. Zdrazil, M., *Collect. Czech. Commun.* **40**, 3491 (1975).
32. Schulz, H., Schon, M., and Rahman, N., *in* “Catalytic Hydrogenation” (L. Cerveny, Ed.), p. 201. Elsevier, Amsterdam, 1986.
33. “Sulphide Catalysts, Their Properties and Applications” (O. Weisser, and S. Landa, Eds.), p. 181. Pergamon, New York, 1963.
34. Carvill, B. T., and Thompson, L. T., *Appl. Catal.* **75**, 249 (1991).
35. Owens, R. J., and Amberg, C. H., *Can. J. Chem.* **40**, 947 (1962).

36. Sullivan, D. L., Ph.D. dissertation, The University of Texas at Austin, 1998.
37. Williams, C. C., and Ekerdt, J. G., *J. Phys. Chem.* **97**, 6843 (1993).
38. Everhardus, R. H., Grafing, R., and Brandsma, L., *J. Royal Neth. Chem. Soc.* **95**, 153 (1976).
39. Korver, P. K., van der Haak, P. J., Steinberg, H., and de Boer, Th. J., *Recl. Trav. Chim.* **84**, 129 (1965).
40. Sauer, N. N., Angelici, R. J., Huang, Y. C. J., and Trahanovsky, W. S., *J. Org. Chem.* **51**, 113 (1986).
41. Sternberg, J. C., Gallaway, W. S., and Jones, D. T. L., *in* "Gas Chromatography" (N. Brenner, J. E. Callen, and M. D. Weiss, Eds.), p. 231. Academic Press, New York, 1962.
42. Aigler, J. M., Brito, J. L., Leach, P. A., Houalla, M., Proctor, A., Cooper, N. J., Hall, W. K., and Hercules, D. M., *J. Phys. Chem.* **97**, 5699 (1993).
43. Chastain (Ed.), Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp., Eden Prairie, MN, 1992.
44. Ramani, N. C., Sullivan, D. L., and Ekerdt, J. G., *J. Catal.* **173**, 105 (1998).