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Deuterodesulfurization of Thiophene: An Investigation of the Reaction Mechanism

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The deuterodesulfurization of thiophene was investigated using selected MoS_2 and reduced molybdenum sulfide (Chevrel phase) catalysts. The extent of deuterium incorporation into thiophene and into specific desulfurization products (hydrogen sulfide, butadiene, and butenes) was determined at 400°C for thiophene conversions near 4%. Unpromoted MoS_2 introduced up to 10 times more deuterium into thiophene than did the promoted catalysts (including the Chevrel phase materials). For all catalysts, H_2S was formed almost exclusively (typically 90+ %), with only small amounts of HDS and D_2S being detected. Except for the unpromoted MoS_2 catalyst, the deuterium distributions determined for the *cis*- and *trans*-2-butene products were nearly identical; the deuterium distribution found for 1-butene was distinct. A mechanism of thiophene hydrodesulfurization can be proposed in which butadiene is the initial desulfurized reaction product. The hydrogen available for hydrogen sulfide formation is derived via hydrogen exchange with thiophene.

INTRODUCTION

While a better understanding of the structure and composition of conventional hydrodesulfurization catalysts has been achieved in recent years, considerable uncertainty remains concerning hydrodesulfurization reaction mechanisms for even simple sulfur-containing organic compounds. Thiophene hydrodesulfurization, for example, has been proposed to involve attack of the carbon–sulfur bond by surface hydrogen, leading to bond breakage and the formation of 1,3-butadiene (*1*). Alternatively, the mechanism has been proposed to involve a dehydrosulfurization process in which hydrogen sulfide is produced by a β-elimination process (*2*). Specifically, the β-hydrogen atoms of thiophene are eliminated to form hydrogen sulfide and diacetylene.

A variety of techniques has been used to study the mechanism of thiophene desulfurization. For example, detailed reaction studies have attempted to compare kinetic parameters for possible mechanisms (*3*). *In situ* spectroscopic studies (*4*) have attempted to elucidate the nature of the species adsorbed on the catalyst surface.

Isotopic tracer studies (using D_2 or ^{35}S) have also been performed. Kieran and Kemball (*5*) found that for MoS_2 catalysts, hydrogen exchange of thiophene occurred primarily at the 2 and 5 positions (α-exchange). Smith *et al.* (*6*) and Behbahany *et al.* (*7*) examined the pulsed-flow deuterodesulfurization of thiophene over Al_2O_3, Mo/Al_2O_3, and CoMo/Al_2O_3 catalysts. Variations in the extent of hydrogen exchange for thiophene were explained in terms of different types of catalytic sites. Cowley (*8*) examined the deuterodesulfurization of 2,5-dideuterothiophene. The hydrogen sulfide produced from 2,5-dideuterothiophene was found to contain more deuterium than that produced from nondeuterated thiophene.

Mikovsky *et al.* (*9*) examined the deuterium isomers of hydrogen sulfide produced

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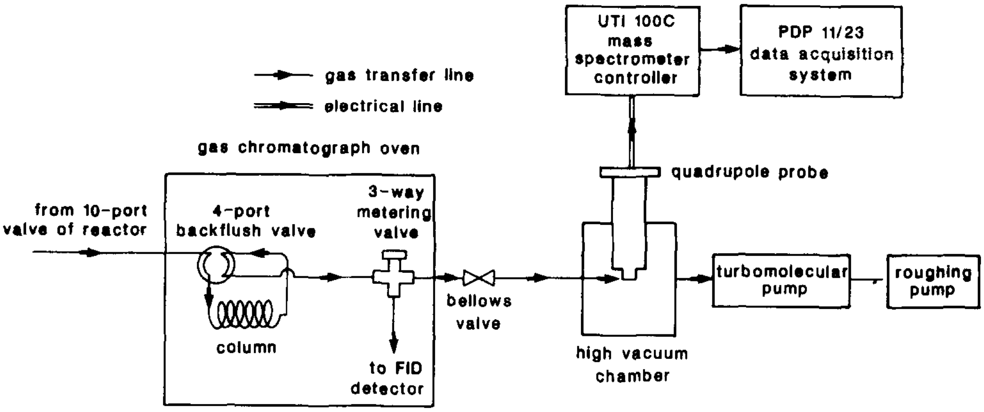

FIG. 1. Experimental apparatus for gas chromatograph/mass spectrometer studies of thiophene deuterodesulfurization.

from the deuterodesulfurization of thiophene in a flow reactor over a commercial $CoMo/Al_2O_3$ catalyst. Interestingly, almost no deuterium was found in the hydrogen sulfide. Blake *et al.* (*10*) examined the isotopic content of hydrogen sulfide, C_4 hydrocarbons, and nondesulfurized thiophene produced from the deuterodesulfurization of thiophene over MoS_2 catalysts in a static reactor. Contrary to the results of Mikovsky *et al.*, the hydrogen sulfide was found to contain almost no protium. Identical deuterium distributions for the butene desulfurization products implied that each product was formed by parallel reaction pathways not involving substantial isomerization.

Gachet *et al.* (*11*) investigated the sulfur content of a commercial $CoMo/Al_2O_3$ catalyst using radioactive ^{35}S as a tracer. These researchers concluded that the sulfur atom derived from the desulfurization of dibenzothiophene was fixed on the surface for some length of time, while an adjacent sulfur atom of the catalyst presumably was released as hydrogen sulfide. Thus, a "turnover" was believed to occur between the sulfur atoms of the catalyst and the sulfur atoms eliminated from dibenzothiophene.

In the work presented here, the deuterodesulfurization of thiophene in a flow reactor using MoS_2-based and Chevrel phase catalysts has been examined. Chevrel phase compounds have been found to be highly active hydrodesulfurization catalysts, while also possessing interesting selectivity properties: low concentrations of hydrogenated products are produced, and differences are observed in the rates of butene isomer production (*12–14*). The isotopic content and deuterium distributions for thiophene and the major desulfurization products (hydrogen sulfide, butadiene, and butenes) were determined in this study.

EXPERIMENTAL

Five catalysts were examined in this investigation: three "large" cation Chevrel phase materials ($Ho_{1.2}Mo_6S_8$, $PbMo_{6.2}S_8$, and $SnMo_{6.2}S_8$), an unpromoted MoS_2 material (referred to as 1000°C MoS_2), and a cobalt-promoted MoS_2 material (referred to as $Co_{0.25}$—Mo_1—S). Details of the preparation and characterization of these materials have been given previously (*14*).

The deuterodesulfurization experiments were performed using the gas chromatograph–mass spectrometer system illustrated in Fig. 1. The reaction products were separated in the column of a gas chromatograph (Antek 300); the flow was then split between the flame ionization detector (FID) of the gas chromatograph and the mass spectrometer (UTI 100C). The FID was used to quantify the concentrations of the individual components of the reactor effluent while the mass spectrometer provided the deuterium distribution for a specific component. An 18-ft. 0.19% picric acid/Carbopack C column was used for product separation. The column did not separate *n*-butane from isobutene; therefore, *n*-butane and isobutene concentrations are reported together.

With only minor modifications, the reactor equipment and procedures were similar to those described previously (*14*). Here, a 6-mm-o.d. fused-silica reactor was used. The empty reactor at 400°C produced a 0.048% conversion of thiophene to C_3 and C_4 hydrocarbons. If the C_3 hydrocarbons and isobutene are neglected, only 0.006% of thiophene was converted to C_4 hydrocarbons. The reactor also had low activity for hydrogen exchange of thiophene; less than 0.003 deuterium atoms/molecule were incorporated into thiophene when using a deuterium–thiophene feed. The ability of the empty reactor at 400°C to hydrogenate, isomerize, or deuterium-exchange a continuous stream of 2% 1-butene in deuterium at a total flow of 22 ml/min was measured. The reactor showed no measurable activity for these reactions.

Catalyst loadings were adjusted to produce thiophene desulfurization conversions of about 4% after 2 h. The $Co_{0.25}$—Mo_1—S, 1000°C MoS_2, and $Ho_{1.2}Mo_6S_8$ materials were stored in a desiccator in air before the exchange measurements. $PbMo_{6.2}S_8$ and $SnMo_{6.2}S_8$ (stored and handled in a nitrogen dry box with no prior exposure to air) were briefly (less than $\frac{1}{2}$ h) exposed to air before being loaded into the reactor and purged with helium. The reactor was heated from room temperature to 400°C in a stream of helium at 19 ml/min (STP). After about 45 min, the helium flow was replaced by a continuous flow of 2 mol% thiophene in deuterium at 22 ml/min (STP). Deuterium (Air Products, Research Guide 99.99%) was metered through a mass flow controller following passage through a copper oxygen removal trap and a 4-Å molecular sieve drying trap. After 20 min and 2, 4, and 6 h, 5 ml of the reactor effluent was sampled and introduced into the gas chromatograph–mass spectrometer system.

In order to minimize cracking of the molecular ions (mass *M*), low ionization energies (18.0 eV, nominal) were used. (The mass spectrometer was equipped with a low energy control circuit [UTI Cat. No. 02042-A].) The mass *M*-1 ion peaks heights, resulting from the loss of one protium atom, were about 9% of the mass *M* molecular ion peak heights for all reaction products. The mass *M*-2 ion peak heights, resulting from the loss of two protium atoms, ranged from 0.17% for H_2S to 0.74% for 1-butene relative to the mass *M* molecular ion peak heights. This low production of *M*-2 ions permitted their presence to be neglected; therefore, corrections were made only for the loss of one hydrogen atom. This correction was done in a statistical manner, assuming equal probabilities for the loss of a protium or a deuterium atom (*15*). Corrections were also made for the presence of naturally occurring heavy isotopes, ^{13}C and ^{34}S.

The "deuterium distribution" was calculated from the mass spectrometer data. Specifically, a series of numbers d_0, d_1, . . . d_m was determined, where d_m represents the fraction of a component containing *m* deuterium atoms. Given these values, calculation of the mean number of deuterium atoms (D.N.) for a component is straightforward:

$$\text{D.N.} = \sum_{i=1}^{N} i d_i$$

Here, *N* equals the number of hydrogen atoms in a molecule.

RESULTS

Table 1 summarizes the deuterodesulfurization results for the various catalysts after 2 h of reaction. Included are the thiophene hydrodesulfurization conversions, the hy-

TABLE 1

Thiophene Deuterodesulfurization Data (after 2 h Reaction)

Catalyst	Thiophene Conversion (%)	Thiophene D.N.	Hydrogen sulfide D.N.	1-Butene		*cis*-2-Butene		*trans*-2-Butene		Butadiene		C_3	Isobutane + Butane (%)
				(%)	D.N.	(%)	D.N.	(%)	D.N.	(%)	D.N.	(%)	
1000°C MoS_2	3.88	1.86	0.053	37.8	5.82	21.6	5.71	28.0	5.59	3.4	4.01	4.0	5.2
$Co_{0.25}$—Mo_1—S	4.36	0.36	0.043	34.2	5.61	24.5	5.77	27.4	5.77	6.8	3.54	5.8	1.3
$Ho_{1.2}Mo_6S_8$	3.68	0.56	0.130	34.8	4.99	23.9	5.05	29.4	5.04	7.3	3.41	2.3	2.3
$PbMo_{6.2}S_8$	4.10	0.17	0.090	55.1	5.36	19.1	5.54	16.8	5.53	6.5	3.59	2.0	0.5
$SnMo_{6.2}S_8$	4.07	0.21	0.060	52.4	5.02	18.3	5.31	20.4	5.26	5.3	3.31	1.9	1.7

drocarbon product distributions, and the mean deuterium numbers (D.N.) for the nondesulfurized thiophene and for the desulfurization products (C_4 hydrocarbons and hydrogen sulfide).

Deuterium Content of Thiophene

A large difference existed between the amount of deuterium incorporated into the nondesulfurized thiophene by the unpromoted and promoted catalysts. 1000°C MoS_2 incorporated 3.3 times more deuterium into thiophene than did $Ho_{1.2}Mo_6S_8$, 5.2 times more than $Co_{0.25}$—Mo_1—S, 8.9 times more than $SnMo_{6.2}S_8$, and 10.9 times more than $PbMo_{6.2}S_8$.

Figure 2 shows the complete deuterium distributions for thiophene in the two extreme cases: 1000°C MoS_2 and $PbMo_{6.2}S_8$. For 1000°C MoS_2, the majority of the thiophene contained 2 deuterium atoms (d_2 = 61.8%); only a small fraction contained no deuterium atoms (d_0 = 1.2%) or 4 deuterium atoms (d_4 = 0.6%). For the other catalysts, the major fraction of the thiophene had no deuterium present (d_0 = 54.3 to 84.5%); a smaller fraction contained 1 deuterium atom (d_1 = 14.4 to 35.9%). Incorporation of 2 (d_2 = 1.1 to 9.6%) or 3 (d_3 = 0.0 to 0.2%) deuterium atoms was much lower and no thiophene fraction contained 4 deuterium atoms.

Deuterium Content of Hydrogen Sulfide

For the five catalysts studied, the hydrogen sulfide product contained an average of only 0.077 deuterium atoms (compared to a possible value of 2). The small amount of incorporated deuterium was present mainly as the HDS isomer (d_1 = 2.5 to 11.1%), rather than as the D_2S isomer (d_2 = 0.7 to 1.2%). This is quite surprising since the reactor feed was composed of 50 mol of D_2 for every mole of thiophene.

Deuterium Content of the C_4 Hydrocarbon Products

The deuterium content of the thiophene desulfurization products (1,3-butadiene, 1-butene, *cis*-2-butene, and *trans*-2-butene) was also determined. All catalysts produced 1,3-butadiene (Table 1); 1000°C MoS_2 produced the least amount (3.4% of the hydrocarbon products), while $Ho_{1.2}Mo_6S_8$ produced the greatest amount (7.3%).

None of the materials produced the ther-

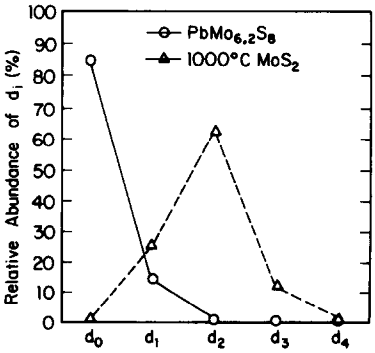

FIG. 2. Thiophene deuterium distribution for 1000°C MoS_2 and $PbMo_{6.2}S_8$ after 2 h reaction.

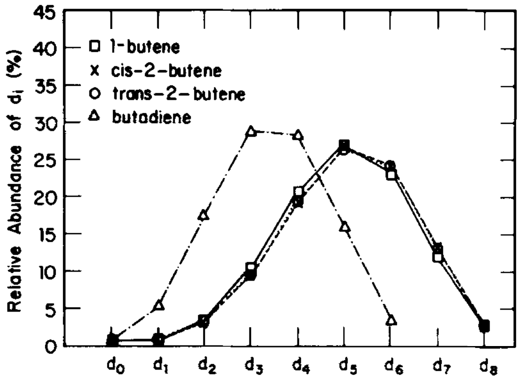

FIG. 3. C_4 hydrocarbon deuterium distribution for $Ho_{1.2}Mo_6S_8$ after 2 h reaction.

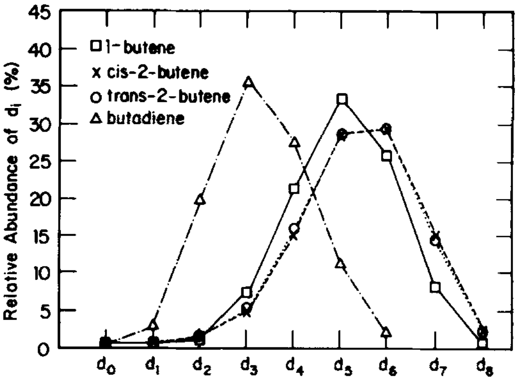

FIG. 4. C_4 hydrocarbon deuterium distribution for $SnMo_{6.2}S_8$ after 2 h reaction.

modynamic equilibrium distribution of the butenes (for 400°C: 26% 1-butene, 44% *trans*-2-butene, and 30% *cis*-2-butene (*16*)). Quite significant differences in the relative concentrations of the butenes were observed. For example, 34.8% of the hydrocarbons produced using $Ho_{1.2}Mo_6S_8$ consisted of 1-butene, compared to 55.1 and 52.4% for $PbMo_{6.2}S_8$ and $SnMo_{6.2}S_8$, respectively.

The average deuterium number for the butenes was 5.71 for 1000°C MoS_2, 5.72 for $Co_{0.25}$—Mo_1—S, 5.03 for $Ho_{1.2}Mo_6S_8$, 5.48 for $PbMo_{6.2}S_8$, and 5.20 for $SnMo_{6.2}S_8$. The deuterium number of butadiene ranged from 4.01 for 1000°C MoS_2 to 3.31 for $SnMo_{6.2}S_8$. The complete deuterium content of the C_4 hydrocarbons are illustrated in Figs. 3, 4, and 5 for $Ho_{1.2}Mo_6S_8$, $SnMo_{6.2}S_8$, and 1000°C MoS_2, respectively.

For all catalysts except 1000°C MoS_2, the *cis*-2-butene and *trans*-2-butene deuterium contents were nearly identical. However, differences existed between the catalysts in the deuterium content of the 2-butenes compared to the deuterium content of 1-butene. For $Ho_{1.2}Mo_6S_8$ (Fig. 3), the 1-butene results were nearly identical to those for both *cis*- and *trans*-2-butene. For $Co_{0.25}$—Mo_1—S, 1-butene contained more d_3 to d_5 species and less d_7 and d_8 species than did the 2-butenes, resulting in a lower deuterium number for 1-butene (D.N. = 5.61) compared to the 2-butenes (average D.N. = 5.77). The differences between the deuterium contents of 1-butene and the 2-butenes were larger than for $PbMo_{6.2}S_8$. The largest difference, however, was observed for $SnMo_{6.2}S_8$ (Fig. 4). For this material, D.N. = 5.02 for 1-butene and D.N. = 5.29 for the average of the 2-butenes.

A significantly different relationship existed for 1000°C MoS_2 (Fig. 5). Here, the *cis*-2-butene and *trans*-2-butene deuterium contents were not as similar, and both differ from 1-butene. Of the three distributions, 1-butene contained the smallest amounts of d_2 to d_5 species and the largest amounts of d_6 to d_8 species. At the other extreme, *trans*-2-butene contained the largest amounts of d_2 to d_5 species and the

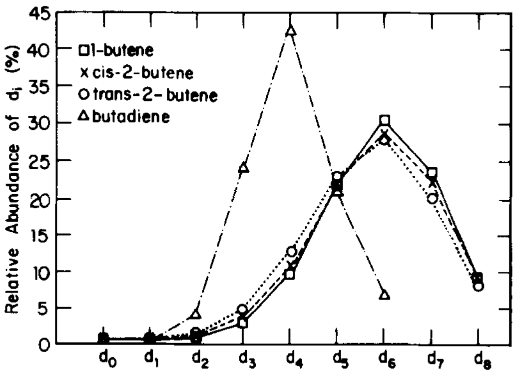

FIG. 5. C_4 hydrocarbon deuterium distribution for 1000°C MoS_2 after 2 h reaction.

smallest amounts of d_6 to d_8 species. Thus, 1-butene had the greatest amount of deuterium (D.N. = 5.82), followed by *cis*-2-butene (D.N. = 5.71) and *trans*-2-butene (D.N. = 5.59).

DISCUSSION

Hydrogen Exchange of Thiophene

At the same thiophene desulfurization conversion levels, the amount of deuterium found in the nondesulfurized thiophene varied by more than a factor of 10 for the five catalysts studied. The greatest extent of hydrogen exchange for thiophene was produced using 1000°C MoS_2—the least active (*14*) and only "unpromoted" catalyst. This implies that the ability of the catalyst to hydrogen exchange thiophene is distinct from the activity for desulfurization.

Hydrogen Sulfide Formation

For all catalysts, almost no deuterium was found in the hydrogen sulfide isomers. After 2 h of reaction (4% conversion), the hydrogen sulfide produced using the five different catalysts contained an average deuterium number of 0.077 out of a possible value of 2. This is in agreement with the flow reactor results of Mikovsky *et al.* (*9*) using commercial $CoMo/Al_2O_3$ catalysts, but is opposed to the static reactor results of Blake *et al.* (*10*) using MoS_2 catalysts. The latter research group found almost no protium in hydrogen sulfide (D.N. = 1.91).

Our results indicate that the protium in hydrogen sulfide must come from thiophene, as this is the only source of protium available. Two possibilities exist:

(1) the protium of hydrogen sulfide comes directly from the thiophene molecule undergoing desulfurization to eliminate the sulfur atom.

(2) The protium of hydrogen sulfide comes not from the thiophene molecule being desulfurized, but from thiophene molecules undergoing hydrogen exchange without desulfurization.

The first possibility is that of the Kolboe intramolecular dehydrosulfurization mechanism in which hydrogen sulfide is removed from thiophene by a β-elimination process to form diacetylene (*2*). The hydrogen of hydrogen sulfide would come directly from the "pure" protium source of the β-carbon positions of thiophene. However, this mechanism is not in accord with the results of Cowley (*8*) who used a labeled thiophene feed (2,5-dideuterothiophene). The deuterodesulfurization of this compound resulted in larger amounts of D_2S (d_2) than was obtained from light thiophene. For the Kolboe mechanism, the deuterium labeling of the α positions of thiophene should have no effect on the deuterium number of hydrogen sulfide. In addition, if the Kolboe mechanism is applied to benzothiophene, formation of unstable benzyne intermediates is required, which clearly are unlikely reaction intermediates (*17*). Thus, the second possible source of protium must be considered: the protium present in hydrogen sulfide is derived from the hydrogen exchange of thiophene. A plausible mechanism needs to be established, however, in which the protium from thiophene becomes associated with the sulfur of hydrogen sulfide.

For the traditional one-point adsorption mechanism of thiophene hydrodesulfurization (*1*), the surface hydrogen attack on the carbon–sulfur bonds results in the formation of butadiene and an adsorbed sulfur atom. (The more recent multipoint adsorption mechanism (*17*), while different in the details of the intermediate stages, reaches this same conclusion.) The adsorbed sulfur atom is known to have an appreciable lifetime on the surface. Gachet *et al.* (*11*) established that there is a "turnover" of surface sulfur atoms in which the sulfur atom of the desulfurized molecule is fixed on the surface while an adjacent atom is presumably removed as hydrogen sulfide. In addition, hydrogen sulfide is known to be strongly adsorbed on hydrodesulfurization catalysts (*18*). This strong adsorption and "turnover" of hydrogen sulfide is also supported by the static reactor results of Blake

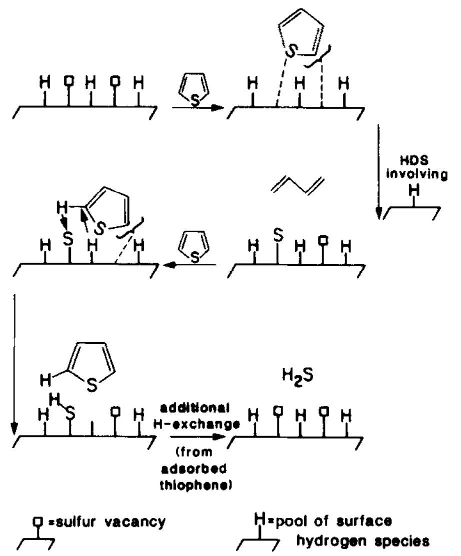

FIG. 6. Proposed mechanism for thiophene desulfurization and hydrogen sulfide formation.

et al.(*19*): thiophene hydrodesulfurization produced half the expected yield of hydrogen sulfide, butanethiol produced one-fourth the anticipated yield, and tetrahydrothiophene produced no hydrogen sulfide at all.

These previous results and the results of this research can be incorporated into a model for the surface reactions. Shown in Fig. 6 is an illustration of the hydrodesulfurization site, which consists of two "adjacent" (presumably sulfur) vacancies. A generalized thiophene adsorption geometry has been indicated since this subject has not been specifically addressed in this research. Reaction of surface hydrogen species with the adsorbed thiophene produces butadiene and an adsorbed sulfur atom.

The "long" surface lifetime of the adsorbed surface sulfur atom allows it to be involved in the hydrogen exchange of thiophene. A thiophene molecule is shown to adsorb on the remaining anion vacancy site in Fig. 6. Hydrogen exchange of thiophene results in the transfer of a protium atom from thiophene to the adsorbed sulfur atom. Upon desorption (for experiments involving D_2 in the feed), a deuterium atom (from a separate source) can possibly become associated with the α-carbon of thiophene, producing the deuterium-containing thiophene. A repetition of this process results in the formation of hydrogen sulfide. The original, multivacancy hydrodesulfurization site is regenerated by the desorption of hydrogen sulfide.

The ability to maintain the multivacancy (or analogously "reduced") site is necessary for high hydrodesulfurization activity. A low ability to desorb sulfur results in a diminished activity for hydrodesulfurization and also causes a greater blockage of the potential hydrodesulfurization sites. These "blocked" sites may be capable of hydrogen exchange with thiophene, but not desulfurization. This is thought to be largely the case for unpromoted catalysts for which the lower ability to desorb sulfur results in a greater activity for the hydrogen exchange of thiophene relative to the activity for thiophene desulfurization.

The conclusion that the hydrogen of hydrogen sulfide originates from the hydrogen exchange of thiophene, rather than the more abundant feed hydrogen (deuterium for deuterodesulfurization), is not surprising considering similar phenomenon for a variety of other catalytic systems. For example, Turkevich *et al.* (*20*) found that the most abundant initial product of the deuteration of ethylenes over nickel wire was C_2H_6 (d_0) rather than the simple addition product $C_2H_4D_2$ (d_2). The rapid, reversible exchange of the hydrogen in ethylene with surface deuterium was thought to populate the surface with protium atoms; these species were involved in the hydrogenation catalysis. In a more closely related experiment, Kieran and Kemball (*21*) established that for the hydrodesulfurization of ethanethiol over MoS_2, a greater proportion of the total surface hydrogen came from the dissociative adsorption of ethanethiol rather than from the direct chemisorption of H_2 or D_2. Fujimoto *et al.* (*22*) examined the liquid phase hydrogenolysis of thiophene using decalin as a hydrogen donor over Co-Mo/carbon catalysts. The hydrogen atoms of decalin were shown to be transferred first to the carbon support and then to the metal sulfide surface, where reaction with thiophene occurred.

C_4 Hydrocarbon Production

The principal hydrocarbon products of thiophene hydrodesulfurization were C_4 hydrocarbons: 1,3-butadiene, 1-butene, *cis*-2-butene, and *trans*-2-butene. The results of this study support the following sequential pathway for producing these hydrocarbons.

thiophene →
butadiene → 1-butene ⇄ *trans*-2-butene
⇅
cis-2-butene

That is, thiophene is converted first to butadiene, which is hydrogenated to primarily 1-butene; isomerization to the 2-butenes then occurs.

Several results support the proposed initial production of butadiene with subsequent hydrogenation.

First, as has been previously reported (*23*), the relative concentration butadiene increases with decreasing conversion, as would be expected for a sequential pathway. After two hours of reaction, for example, the amount of butadiene produced over two independently examined 1000°C MoS_2 samples increased by a factor of 5.4 (from 3.4 to 18.4%) when the conversion decreased from 3.88 to 0.77%. In contrast, the relative amount of 1-butene remained essentially unaltered (37.8% versus 33.8%), while the concentration of *cis*-2-butene (21.6% versus 10.9%) and *trans*-2-butene (28.0% versus 12.5%) declined upon lowering the conversion level. Similar results were obtained for the other catalysts.

Second, butadiene is also known to be readily hydrogenated to butene over hydrodesulfurization catalysts. This rate is generally greater than the rate of thiophene or tetrahydrothiophene hydrodesulfurization (*19*). Butadiene hydrogenation can also result in the production of a thermodynamic excess of 1-butene, as was found here for the desulfurization of thiophene (*10*).

Several results are also useful in establishing that 1,3-butadiene is hydrogenated to give primarily 1-butene, which is then isomerized to produce the 2-butenes.

First, all catalysts produced concentrations of 1-butene is excess of the thermodynamic equilibrium levels (Table 1). The catalysts with the least ability to isomerize 1-butene gave the largest relative amounts of 1-butene. For example, $PbMo_{6.2}S_8$ and $SnMo_{6.2}S_8$ have shown little ability to isomerize 1-butene/hydrogen pulses (*14*). These materials produced 1-butene in great excess during thiophene hydrodesulfurization.

Second, the deuterium distributions of the 2-butenes were different from 1-butene. For all catalysts except 1000°C MoS_2, the *cis*-2-butene and *trans*-2-butene deuterium distributions were nearly identical, but they were distinct from that for 1-butene. In proceeding from $Ho_{1.2}Mo_6S_8$ to $Co_{0.25}$—Mo_1—S to $PbMo_{6.2}S_8$ to $SnMo_{6.2}S_8$, the 2-butenes contained increasingly more deuterium than did 1-butene. The greater deuterium content resulted from the added surface interactions involved in the reaction sequence.

$Ho_{1.2}Mo_6S_8$ had demonstrated a high isomerization activity for 1-butene/hydrogen pulses (*14*). In addition, the butene distribution produced from thiophene hydrodesulfurization was close to equilibrium values. This high isomerization ability led to a rapid interconversion of the butenes and nearly identical butene deuterium distributions. The low isomerization ability of $PbMo_{6.2}S_8$ and $SnMo_{6.2}S_8$, in contrast, resulted in distinct deuterium distributions for the 2-butenes and 1-butene.

CONCLUSIONS

The presence of a promoter in molybdenum-based catalysts greatly decreases the ability of the catalyst to hydrogen exchange thiophene relative to the ability to desulfurize thiophene. For all catalysts under continuous flow reactor conditions, the hydrogen in hydrogen sulfide (derived from thiophene hydrodesulfurization) comes from thiophene molecules undergoing hydrogen exchange and not from the gas phase hydrogen source.

Comparison of the hydrocarbon product distributions for the different catalysts indicates that 1,3-butadiene is the initial product of thiophene desulfurization. The diolefin is hydrogenated primarily to 1-butene, which then is isomerized to the 2-butenes.

In all aspects of thiophene deuterodesulfurization, the Chevrel phase catalysts tend to behave in a manner which is more similar to cobalt-promoted MoS_2 catalysts than to unpromoted MoS_2 catalysts.

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