

CATALYTIC HYDRODESULFURIZATION OF THIOPHENE
VI. COMPARISONS OVER MOLYBDENUM DISULFIDE, COBALT MOLYBDATE,
AND CHROMIA CATALYSTS¹

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ABSTRACT

The hydrodesulfurization of thiophene over five molybdenum disulfide catalysts, an alumina-supported cobalt molybdate, and a chromia catalyst has been investigated. Comparisons on the basis of equal surface areas showed that desulfurization activity did not vary a great deal. It was established mainly by working at very low conversion levels that 1,3-butadiene was a product over all these catalysts, and that a mixture of butadiene, the three *n*-butenes, and *n*-butane constituted the actual *primary* reaction product. The reaction rate is strongly dependent on conversion, probably as the result of small quantities of product H₂S, the rate decreasing by a factor of 100 in going from 0.01% to 5% conversion in a typical flow experiment. A strong enhancement of the rate over MoS₂ was noted in the presence of oxygen.

INTRODUCTION

Following a series of studies of the hydrodesulfurization of thiophene over cobalt molybdate catalysts previously carried out in this laboratory (1-3) it was found to be of interest to investigate the catalytic properties of molybdenum disulfide itself, as this may well be the most important constituent in the sulfided cobalt molybdate.

Most of the experiments to be described below were carried out in the steady state and using much lower reaction rates than before; for this reason some comparative measurements using alumina-supported cobalt molybdate and pure chromia were included, these being the catalysts employed in the previous studies (1-5).

EXPERIMENTAL

(i) Apparatus

Modifications of the flow system which has been previously described (1) made it possible to pass a complete range of H₂/He mixtures through a thiophene saturator at flow rates varying from 1 to 200 ml/min at or near atmospheric pressure, flows and pressures being measurable with 1% precision or better. As before, pulse injection into a system in the steady state could take place from a syringe through a serum cap at the top of the microreactor. In addition, a simple syringe holder has been constructed, which permits additions to be sufficiently slow so that new steady states can again be attained over periods of several minutes. This is done by moving forward the plunger of the syringe with a screw (1 mm per turn) continuously or intermittently, depending on the requirements of a particular system. For the analysis of tail gases, when they are not passed directly to the gas chromatographic column, a commercial sampling valve (Perkin-Elmer) has now been incorporated in the apparatus.

The range of the apparatus was considerably extended by adding a flame ionization detector as an alternative to the Gow-Mac thermal conductivity detector. The flame ionization detector was a copy of one previously used by one of us (S. Kolboe, Unpublished). Using this combination of detectors, product concentrations from 3×10^{-12} up to 5×10^{-6} mole/ml (5×10^{-5} to 80 torr) were measurable; combined with the full range of flows available, reaction rates (product concentration \times flow rate) from 5×10^{-14} to 1×10^{-3} mole/s were attainable, and these then represented the extreme limits of the apparatus.

An 8 ft propylene carbonate column (25% w/w) for C₄ analysis was used at 0 °C, the temperature being somewhat lower than that used earlier to minimize "bleeding" from the stationary phase, and a 6 ft squalane column (25% w/w) at 80-100 °C was again used for the analysis of sulfur compounds.

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(ii) Catalysts

I. MoS₂- "Molykote", a finely divided solid lubricant, used as received.

II. MoS₂ (Anachemia), as received.

III. Catalyst II doped with 1 mole % cobalt. Prepared by making a slurry with an aqueous solution of cobalt nitrate, drying, outgassing at 400–500 °C and then heating in a sealed quartz ampoule to 650 °C for 4 h.

IV. MoS₂ made by heating MoS₃ to 400 °C in a H₂/He mixture (6).

V. Prepared by heating catalyst IV to 650 °C for 1 h in a H₂/He mixture.

VI. Prepared by heating catalyst V to 800 °C for 12 h in a sealed quartz ampoule.

Although no changes in activity were observable in catalysts I–VI after the first 1 to 2 h of desulfurization at 300 °C, measurements were not made until after the first 5–10 h to ensure constant activity.

VII. Cobalt molybdate on alumina, Girdler No. G35A (1) crushed from pellets and using –65 mesh portion. Contains 1.3% Co + 6.1% Mo. Activated by heating in hydrogen to 400 °C and then stabilized (i.e. sulfided) with thiophene and H₂ for 16 h at a flow rate of 5 ml/min.

VIII. Chromia gel. Prepared by slowly adding a 10% ammonia solution to a 20% Cr(NO₃)₃ solution until pH = 9.0, filtering, washing, and drying.⁴ Activated by slowly heating to 400 °C in hydrogen, and stabilized like catalyst VII.

The B.E.T. surface areas as well as spectrographic analyses of the catalysts are shown in Table I. The percentages given are an indication of order of magnitude only.

TABLE I
B.E.T. surface areas and semiquantitative spectrographic analysis of catalysts

Catalyst	I	II	III*	IV	V	VI	VII	VIII
Area (m ² g ⁻¹)	2.2	3.3	3.3	157	67	12	241	150
% Mg	0.005–0.05			0.0005–0.005			—	0.001–0.01
% Mn	0.005–0.05			None			—	None
% Pb	0.01–0.1			0.001–0.01			—	0.005–0.05
% Si	0.1–1			None			—	0.05–0.5
% Fe	0.1–1			None			—	0.05–0.5
% Ge	0.01–0.1			None			—	None
% Bi	0.05–0.5			None			—	0.005–0.05
% Al	0.05–0.5			None			—	0.001–0.01
% Cu	0.05–0.5			0.001–0.01			—	0.0001–0.001
% Ag	0.001–0.01			0.005–0.05			—	None
% Ca	0.01–0.1			None			—	0.005–0.05
% Ni	None			None			—	0.001–0.01

*1% Co not shown in table.

All catalysts gave reproducible results and nos. I, II, III, V, VI, and VII showed no decrease in activity after being in use for 2 to 3 weeks.

(iii) Reagents

Thiophene, Eastman; this contained some C₄ impurities which were largely removed by bubbling dry air through the liquid until about one-third of it had evaporated. Any C₄ compounds remaining were negligible even for measurements at very low conversion. The other impurities have been reported in (2).

C₄ hydrocarbons, Phillips research grade; used as received. Hydrogen, Matheson Ultrapure; used as received. Helium, Matheson; dried over Anhydrone.

RESULTS AND DISCUSSION

In contrast to the work reported previously in this series, conditions were now chosen so as to achieve much lower reaction rates and conversions in order to avoid the complications arising from secondary reactions. This was made possible by the increase in analytical sensitivity and it was also, in part, facilitated by using low-area catalysts.

No appreciable cracking was noted for any of the catalysts, and quantities of isobutylene and isobutane formed were negligible. There was no indication of any polymerization of unsaturated hydrocarbons. The product distribution of the *n*-C₄ hydrocarbons depended greatly on the catalyst and the conditions of a given experiment.

⁴A sample of this catalyst was kindly provided by Dr. Y. Amenomiya.

Attempts to run the reactor under differential conditions failed because of the extremely strong dependence of reaction rate on conversion even down to very low conversions, as shown in Fig. 1 for all catalysts. This strong dependence on conversion is believed to be caused by the H_2S formed in the reaction. Hydrogen sulfide addition experiments have shown that this gas strongly depresses the reaction rate. The effect appears to be of the right magnitude for explaining the conversion behavior; unfortunately it has not been possible to reproduce the curves shown in Fig. 1 by independent H_2S additions, because

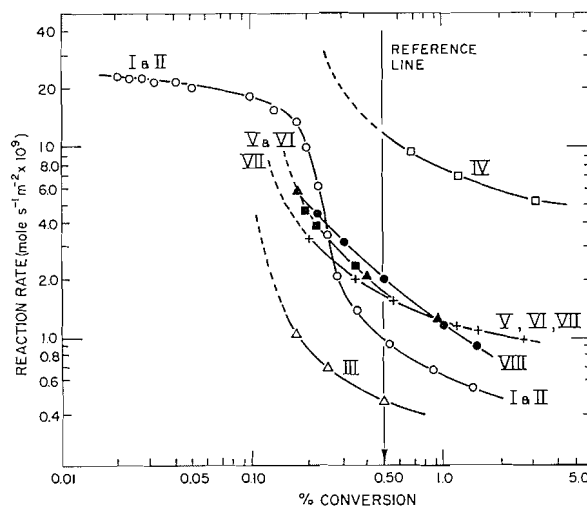


FIG. 1. Thiophene desulfurization as a function of conversion over various catalysts at 288 °C. Partial pressures: thiophene 20 torr; hydrogen 740–770 torr. Flows ranged from 2 to 200 ml/min, catalyst weights from 6 mg to 1.5 g. Roman numerals correspond to catalyst numbers. Extrapolations shown are based on measurements at 10–20 °C lower temperatures (identical curve shapes).

the required concentrations would have to be too small (the partial pressures of H_2S would have to lie in the region 0.02 to 0.2 torr). It has been possible to eliminate from consideration the effects of diffusion in the gas phase or in catalyst pores, temperature gradients within porous catalyst particles or from catalyst surface to ambient, as well as C_4 -hydrocarbons generated by complete desulfurization of the 0.02% butanethiol impurity present in the thiophene. This was done by calculations and some ancillary experiments, such as employment of constant weight-to-flow ratios for different weights of catalyst.

It can be seen from Fig. 1 that unambiguous comparisons of catalyst activity cannot be made. However, for approximate comparisons under the same experimental conditions a region in which the curve shapes are similar has been arbitrarily selected (see "Reference Line" at 0.5% conversion); these comparative rates have been assembled in Table II. The most striking fact emerging from that table is the relatively slight variation of activities based on unit surface area of catalyst (column 5), particularly when compared with the rates based on unit weight of catalyst which vary by three orders of magnitude (column 4). This can be considered significant despite the uncertainties in the comparison of different catalysts discussed in connection with Fig. 1. Unless one makes the usual assumption that for the supported cobalt molybdate, VII, substantial coverage of the alumina surface has resulted from the impregnation processes employed, the good agreement in that case must be regarded as fortuitous. We are confident, however, that the assumption is correct and the comparison justified. The similarity in rates of desulfurization over all the catalysts

TABLE II

Reaction rates at 0.50% conversion and 288 °C. Hydrogen and thiophene pressures: 740 and 20 torr respectively; hydrogen flow rate: ~20 ml/min. Catalyst amounts varied from 10 mg to 1.5 g to give a total surface of 2-5 m²

No.	Type	B.E.T. area (m ² g ⁻¹)	Reaction rate	
			(10 ⁹ molc s ⁻¹ g ⁻¹)	(10 ⁹ mole s ⁻¹ m ⁻²)
I	MoS ₂ (Molykote)	2.2	2.2	1.0
II	MoS ₂ (Anach.)	3.3	3.0	0.90
III	MoS ₂ + 1% Co	3.3	1.65	0.5
IV	MoS ₂ from MoS ₃ (400°)	154	1 600	11
V	IV (650°)	67	107	1.6
VI	IV (800°)	12	18	1.5
VII	Cobalt molybdate on alumina (Girdler G35A)	241	400	1.65
VIII	Cr ₂ O ₃	150	300	2.0

is strongly suggestive of the same basic mechanism being operative in all cases. In this connection it may be noted that an apparent activation energy of 24 kcal/mole was determined over catalyst V (MoS₂) in agreement with previously published values of 25 kcal/mole over VII (1) and 24 kcal/mole over a Cr₂O₃ catalyst (4) similar to VIII.

It is interesting to note, in passing, the decrease in activity per unit area when catalyst IV was pretreated by reduction in a H₂/He mixture at a higher temperature (catalyst V, 650°). In view of the common origin of the catalysts this decrease can be considered significant. It could be due to improved reduction, or to thermal destruction of unstable surface states in the MoS₂ crystallite, of surface impurities, or of micro-cracks accessible only to N₂; or combinations of these factors. Further sintering (catalyst VI, 800°), although decreasing the surface area by a factor of more than 5, had virtually no effect on activity per unit area or in other words on the catalytic nature of the surface.

The present set of experiments has thrown new light on the distribution of C₄ hydrocarbons over the various catalysts. Previously, both the *n*-butenes and *n*-butane had been identified as reaction products over a cobalt molybdate identical with catalyst No. VII (1), as well as over a chromia similar to No. VIII (4); moreover, butadiene had been found over chromia, and identified on catalyst VII during infrared studies carried out while the reaction was in progress (R. A. Siddiqui and C. H. Amberg. Unpublished). It had been assumed at the time that butadiene would occur in the gas phase also over the cobalt molybdate catalyst in significant amounts, but that it was being hydrogenated too fast for detection. Butadiene has now been definitely identified as a gas phase product over all the catalysts used.

Even though the C₄ distribution depends strongly on conditions, a single set is given in Table III for the same conditions as those specified in Table II for purposes of comparison.

In the earlier experiments in this series, the distribution of the *n*-butenes had always been close to equilibrium (1), although a tendency for 1-butene and *cis*-2-butene to occur slightly in excess had been observed (3). Present conditions of steady-state operation at very short contact times strongly accentuate this tendency, so that the distributions are far from equilibrium. Thus it can be calculated from Table III that the observed quantity of 1-ene exceeded the equilibrium value by factors of 3-6 (equilibrium distribution: 13.2% 1-ene, 32.2% *cis*-2-ene, 54.6% *trans*-2-ene).

The dependence of C₄ distribution on conversion can be appreciable even at conversions as low as 0.5%; this is borne out by Fig. 2, which is shown as an example. Care should be

TABLE III

Distribution of C₄ hydrocarbons from thiophene at 0.50% conversion and 288 °C. Hydrogen and thiophene pressures: 740 and 20 torr, respectively; hydrogen flow rate: ~20 ml/min

Catalyst	Butadiene (%)	1-Butene (%)	<i>cis</i> -2-Butene (%)	<i>trans</i> -2-Butene (%)	Butane (%)
I	6.2	42.6	21.7	22.0	9.1
II	6.9	42.5	22.3	19.2	8.8
III	8.4	55.6	14.0	17.4	4.7
IV	7.2	39.9	16.7	23.5	12.7
V	4.0	28.5	22.0	36.5	9.5
VI*	—	—	—	—	—
VII	2.2	47.5	19.8	24.3	6.2
VIII	7.7	31.3	11.8	11.8	37.4

*Product distributions for catalyst VI were only roughly surveyed, but did not appear to show significantly different trends.

taken not to extrapolate the curves in Fig. 2 to zero conversion, because in the interval not shown here, abnormal and yet completely reproducible inflections of the curves have been observed for some catalysts, for which we have at present no reasonable explanation. Catalysts IV, V, VI, and VII exhibited essentially the same dependence upon conversion as is demonstrated in Fig. 2, while catalysts I, II, III, and VIII varied to a lesser extent with conversion.

Consecutive reactions—if by this we mean further reaction with a product molecule which has been present in the gas phase—were found not to be the prime reason for the changing product distribution with conversion. Thus the isomerization and hydrogenation rates of 1-butene over catalyst V were examined by slowly admitting the gas to the reactor, simultaneously with the thiophene, and under the same conditions as were indicated for Fig. 2 except for a conversion level of 0.4%. It had been shown previously that olefins do

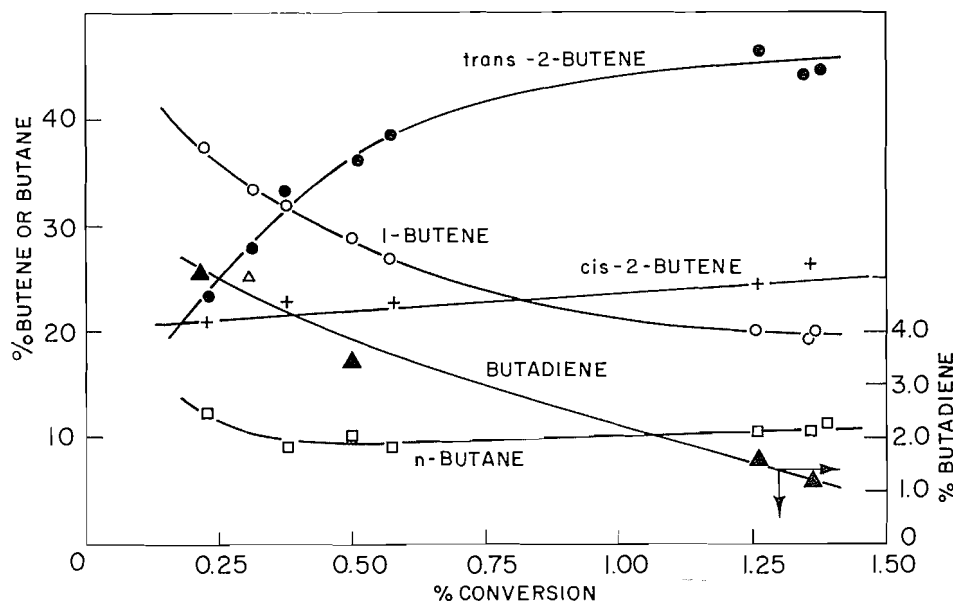


FIG. 2. Product distribution as a function of thiophene conversion over MoS₂ catalyst V at 288 °C. Partial pressures: thiophene 20 torr; hydrogen 740 torr. Flows 5–200 ml/min. Catalyst weights 20 and 75 mg.

not much affect the rate of hydrodesulfurization (1) and, in any case, the concentration of the added 1-butene was only about 1% of that of the thiophene. In this way no more than 1-2% of the added 1-butene was isomerized to *cis*- or *trans*-2-butene, the isomerization following first-order kinetics. No hydrogenation of the added butene could be detected. From somewhat different experiments performed with butadiene on the other hand one may deduce that a fair amount of gas-phase butadiene, say between 25 and 50%, would be hydrogenated under the above conditions. It must then be concluded that distributions of the type shown in Fig. 2 are essentially primary product distributions of the C₄ hydrocarbons as desorbed from the catalyst, the only exception being the fast reacting butadiene which shows too low a value. Considering that no hydrogenation of butene could be detected, it is remarkable that the fully hydrogenated butane forms a significant fraction of the reaction products. Since the other catalysts exhibited the same reaction pattern it can be stated that all of them yield a *primary* product consisting of a mixture of 1,3-butadiene, the three *n*-butenes, and *n*-butane. This result had been anticipated by an indirect calculation using data from experiments over chromia (4).

The fact that 1,3-butadiene was identified over all our catalysts (in amounts of up to 60%, depending on conditions) might indicate, as has been argued previously, that it is the first C₄-hydrocarbon formed from thiophene. If this is so, however, it can now be seen that only a part of the butadiene molecules can have desorbed from the surface prior to further hydrogenation. This is borne out by the following experiments over catalyst No. I: Butadiene was admitted to the system which was in the steady state with respect to thiophene desulfurization. The distribution of the butenes coming from the added butadiene was evaluated and found to be similar to that arising from thiophene desulfurization, but significantly lower in 1-butene (Table IV).

TABLE IV

Product distributions from thiophene and from added 1,3-butadiene over catalyst No. I at 320 °C and 1.5% conversion. Partial pressures: thiophene 20 torr, H₂ 200 torr, He 540 torr; flow rate of hydrogen/helium carrier gas: 20 ml/min; catalyst weight: 1.5 g

Reactant	1-Butene (%)	<i>cis</i> -2-Butene (%)	<i>trans</i> -2-Butene (%)	Butane (%)
Thiophene	50.0	19.0	25.5	5.8
Thiophene (butenes only)	(53)	(20)	(27)	
1,3-Butadiene*	40	22	37	<0.5

*Mean of two experiments in which amount of butadiene added was, respectively, equal to and three times the total C₄ yield from thiophene.

The table shows that the behavior of butadiene is analogous to that of 1-butene, in that complete hydrogenation of the free gas can be almost totally suppressed under conditions in which thiophene desulfurization can still give rise to significant amounts of butane, provided these conditions are appropriately selected. Similar results were observed over catalyst V, which leads us to believe that the phenomenon is a general one for all our catalysts.

If we accept that the first C₄-hydrocarbon product from thiophene is adsorbed 1,3-butadiene, then the different product distributions from thiophene and from added butadiene shown in Table IV can only arise from two different surface configurations of the adsorbed butadiene molecule. Similar reasoning would apply to butenes from thiophene on the one hand, and butenes added or derived from hydrogenated butadiene on the other, if

and only if the hydrogenation route of thiophene proceeds through adsorbed butene. This is so, because thiophene can be made to yield butane under conditions where gas phase butene will not hydrogenate further. The above arguments are not invalidated by the possibility of a sulfur-containing adsorbate, say of the type



preceding the butadiene, if the latter is to be regarded as an intermediate member of the hydrogenation sequence (3). However, if butane were to be formed directly from the adsorbed diene-thiol a much more complex desulfurization mechanism than had been envisaged so far would have to be proposed. This will be discussed in a later publication (S. Kolboe. To be published).

It was noted previously that olefin hydrogenation was strongly suppressed in the presence of H_2S over supported cobalt molybdate (catalyst VII), and to a much lesser extent over chromia (4). The selective effect of H_2S has now been observed over pure MoS_2 (catalyst VI) and so may be assumed to be general for MoS_2 catalysts. The fact that butadiene was always fully hydrogenated to butenes and butane in the earlier studies was due to the very different reaction conditions employed then.

In an effort to reexamine the poisoning effect of ammonia on the desulfurization reaction (3) a $10 \mu\text{l}$ pulse of conc. aqueous NH_3 was injected into a steady-state system operating over catalyst IV (100 mg catalyst; 250°C ; hydrogen flow: 25 ml/min; partial pressure of thiophene: 20 torr). No effect whatever could be found after 2 min. On examining the hydrogenation and isomerization of 1-butene (pulse addition) in the absence of thiophene but otherwise under similar conditions over catalyst VI, an effect was observed with ammonia solution, but this lasted only about 10 min; moreover, water addition produced a similar effect. As before, H_2S acted as a much stronger and long-lasting poison.

The above observations indicate that the activity of pure MoS_2 does not reside in acid sites of the Brønsted type: one would not expect fast desorption of NH_3 from such sites at the relatively low temperatures employed. This is in contrast to the strong and persistent effect of pyridine found earlier with the cobalt molybdate on alumina catalyst (3). If the earlier results are to be interpreted on the basis of acid-site poisoning in the Brønsted sense—as was implied at the time—then it becomes necessary to invoke cooperative effects arising from the acidic sites of the alumina. This would be compatible with the fact that only a partial poisoning of the supported catalyst was observed. Obviously, however, a

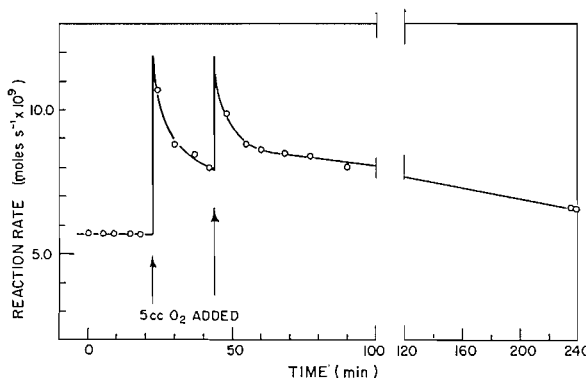


FIG. 3. Effect of oxygen pulses on the rate of desulfurization of thiophene over MoS_2 catalyst V at 289°C and 1.2% conversion. Partial pressures: thiophene 20 torr; hydrogen 740 torr. Flow 21 ml/min. Catalyst weight 75 mg.

more detailed study is required before specific sites can be identified with any degree of confidence.

Finally it is worthy of note that oxygen addition, as demonstrated in Fig. 3, led to an immediate doubling of the desulfurization rate over catalyst V, followed by gradual return to the initial rate over a period of hours. At the same time the product composition was completely unchanged, indicating that desulfurization and hydrogenation sites, if distinct from each other, were affected to the same extent. Isomerization was too close to equilibrium for significant conclusions to be drawn regarding the sites pertinent to that reaction. Similar experiments performed during butene hydrogenation resulted in the same qualitative behavior, but the effect was much more marked in that the hydrogenation rate was increased by a factor of 50-100. We have at present no explanation of these results. However, since oxygen is a strong electron acceptor, it is tempting to find an answer in terms of the electronic properties of MoS_2 which is to be regarded as a semiconductor. An indirect promotion through water formation can probably be ruled out, because under all conditions which were tried water was found to act as a poison.

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