

CATALYTIC METHODS FOR OBTAINING THIOPHENE AND  
ALKYLTHIOPHENES FROM PETROLEUM REFINING PRODUCTS  
AND SULFUR-CONTAINING ORGANIC COMPOUNDS

M. A. Ryashentseva, Yu. A. Afanas'eva,  
and Kh. M. Minachev

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This review is devoted to catalytic methods for obtaining thiophene and alkylthiophenes from  $C_2$ - $C_6$  hydrocarbons and from various organosulfur compounds - aliphatic sulfides, mercaptans, alkylthiophenes, thiophane, and sulfones. Multicomponent chromium-containing catalysts have considerable activity in the majority of the reactions. The catalytic method for obtaining thiophene and alkylthiophenes by the reaction of  $C_2$ - $C_6$  hydrocarbons with hydrogen sulfide may be the most promising one.

### Introduction

Owing to their high reactivities, thiophene and its homologs are potential raw materials for obtaining the most diverse compounds of both the aliphatic and alicyclic series. Methods for the synthesis of several polyorganosiloxanes, herbicides, physiologically active and aromatic substances, yeast-growth stimulators, etc., have been created on the basis of thiophene. However, the assimilation of these research efforts in industry is complicated by the absence of accessible methods for obtaining thiophene and alkylthiophenes. In the Soviet Union, thiophene is currently obtained only from the benzene fraction of coal tar, and this source will not be able to satisfy the increasing requirements of the national economy.

An industrial apparatus for the preparation of thiophene from  $C_4$  hydrocarbons and molten sulfur at temperatures up to  $700^\circ$  and atmospheric pressure has been put into operation in the United States as a result of intensive research [1-9]. In addition to the high temperature, another disadvantage of this method is the considerable resinification that occurs. A catalytic process based on the reaction of hydrocarbons with sulfur dioxide or hydrogen sulfide or on the conversions of diverse sulfur-containing organic compounds seems more expedient. It should be pointed out that most of the systematic investigations relative to the catalytic synthesis of thiophene and alkylthiophenes were carried out in the Soviet Union in the sixties.

In this review we discuss material on the catalytic methods for obtaining thiophene and alkylthiophenes by heterocyclization of aliphatic hydrocarbons with sulfur dioxide or hydrogen sulfide, by dehydrocyclization of dialkyl sulfides, by dealkylation of alkylthiophenes, by dehydrogenation of thiophane, and by hydrogenation and dehydrogenation of sulfones.

### Catalytic Synthesis of Thiophene and Alkylthiophenes by the Reaction of $C_2$ - $C_6$ Hydrocarbons with Sulfur Dioxide or Hydrogen Sulfide

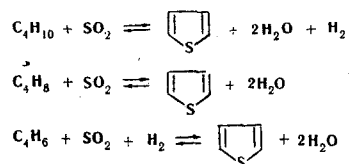
Studies on the use of sulfur dioxide in the synthesis of thiophene were begun 20 years ago and continue to attract the attention of researchers in various countries. The possibility of obtaining thiophene and alkylthiophenes [10, 11] from sulfur dioxide and aliphatic hydrocarbons is due to the presence of no less than four carbon atoms in the straight chain of the latter. In fact, the synthesis of thiophene from sulfur dioxide and ethane [12, 13], ethylene [10, 13, 14], and propylene or isobutane [10] could not be accomplished.

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The formation of thiophene from sulfur dioxide and C<sub>4</sub> hydrocarbons is observed as a result of the following reactions:



The literature data on the catalytic synthesis of thiophene from sulfur dioxide and C<sub>4</sub> hydrocarbons published before the sixties primarily involve patents [12-20]. The single exception was a study [10] in which there was a detailed description of the method of synthesis of thiophene from a number of aliphatic hydrocarbons at high temperatures and atmospheric pressure on various catalysts. However, the method used to prepare the catalyst was not pointed out, and information regarding their stability was also absent.

The most efficient and frequently used catalysts in the synthesis of thiophene from sulfur dioxide and hydrocarbons are aluminum oxide-based catalysts that contain oxides or sulfides of group V and VI metals (molybdenum, tungsten, and chromium). Silica gel, aluminum oxide, active charcoal, and clays can also be used as catalysts.

The formation of thiophene from butylene proceeds with higher yields and under milder temperature conditions than from n-butane. The maximum yield of thiophene from n-butane (43%)\* is achieved on an aluminum-molybdenum catalyst [15], while the maximum yield from butylene (60%) is obtained on a catalyst containing 2% BaO, 15% CuCrO<sub>2</sub>, and 83% Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> [20]. Up to 62 and 75% thiophene, respectively, can be obtained in a fluidized bed from sulfur dioxide and n-butane [15] or butylene [17] on an aluminum-chromium catalyst.

Various modifications of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and multicomponent catalysts based on it were investigated as catalysts in [21-29]. Aluminum oxide calcined at 1000° has the greatest activity; when it is used, the yield of thiophene from sulfur dioxide and n-butane or butylene was 44 and 55%, respectively. X-ray diffraction analysis demonstrated that this sample corresponds to high-temperature  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. If chromium oxide, molybdenum oxide, or, simultaneously, chromium oxide and potassium oxide are introduced into the  $\gamma$ -aluminum oxide [28], an increase in its activity can be observed. The introduction of rare-earth-element oxides into aluminum oxide and chromium- and molybdenum-containing catalysts results in a decrease in their reactivities. Thus it was demonstrated in these studies that multicomponent catalysts have lower activity than aluminum oxide calcined at 1000° in the synthesis of thiophenes from C<sub>4</sub> hydrocarbons and sulfur dioxide. However, the yields of thiophene obtained in the presence of the latter constitute only 20-33% of the equilibrium yields [25, 29].

The literature on the synthesis of thiophene homologs by the reaction of sulfur dioxide with C<sub>5</sub>-C<sub>6</sub> hydrocarbons is limited [10-12, 15, 17, 18, 30, 31]. The reactions were studied principally in the presence of an aluminum-chromium catalyst, except for [30, 31], in which the oxides of magnesium and calcium [30] and the oxides of aluminum and neodymium [31] were used as catalysts. In addition to alkylthiophenes, thiophene is also present in the products of the reaction of sulfur dioxide with hydrocarbons with more than four carbon atoms, probably as a result of the reaction of sulfur dioxide with the products of cracking of the starting hydrocarbon or as a consequence of dealkylation of the alkylthiophenes. When the number of carbon atoms in the molecule of the starting hydrocarbon increases from four to six, the yields of the thiophene compounds from the reaction of sulfur dioxide with hydrocarbons decrease, which is apparently associated with the increase in the number of possible reactions. Thus, for example, dehydrocyclization to form benzene is more favorable for C<sub>6</sub> hydrocarbons of normal structure than the reaction to form a heterocycle, since the conjugation energy of benzene is 36 kcal/mole as compared with 28 kcal/mole for thiophene [32].

Branching of the carbon chain of C<sub>5</sub>-C<sub>6</sub> paraffin hydrocarbons has only a slight effect on the yield of thiophene compounds. The optimum temperature for conversion of C<sub>5</sub>-C<sub>6</sub> isoalkenes to the corresponding alkylthiophenes is 150-250° lower than the temperature required for the conversion of n-butane, butylene, and 1,3-butadiene [11].

\* Here and elsewhere, the yield is given in weight percent based on the hydrocarbon passed through the system.

The use of hydrogen sulfide as one of the starting substances for the synthesis of thiophene from acetylene and hydrogen sulfide on aluminum oxide at 400-450° was initiated in 1915 by Chichibabin [33, 34]:

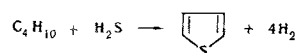


Subsequent investigators [35, 36] could not reproduce his results, probably as a result of differences in the catalyst samples used. Mercaptans, benzene, carbon disulfide, etc., are formed along with thiophene and its homologs in the reaction of acetylene with hydrogen sulfide. Reviews of studies accomplished up to 1952 with respect to the catalytic synthesis of thiophene from hydrogen sulfide and acetylene can be found in [37, 38].

According to the data in [39, 40], thiophene is obtained in a 50-52% yield in the presence of industrial-grade A-1  $\gamma$ - $\text{Al}_2\text{O}_3$  from hydrogen sulfide and an electrical cracking gas containing 29.0 acetylene, 7.8 ethylene, 0.6 ethane, 5.6 methane, and 57.0 vol.% hydrogen under the conditions found for the catalysis.

Until recently, only a single example [41] of the synthesis of thiophene from n-butane and hydrogen sulfide in 31.2% yield on a 10%  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalyst was known.

The results of systematic investigations for the selection of active, selective, and stable oxide catalysts in the synthesis of thiophene from  $\text{C}_4$  hydrocarbons and hydrogen sulfide are presented in [23-27, 29, 42-47]. Multicomponent catalysts based on aluminum oxide that contains oxides of the transition metals (chromium and molybdenum), oxides of rare-earth elements (neodymium and lanthanum), and potassium oxide were investigated as catalysts. The selection of the optimum composition of the catalyst and conditions for the synthesis of thiophene was made in the case of the reaction of hydrogen sulfide with n-butane:



It was shown that various modifications of aluminum oxide and aluminum oxide containing rare-earth-element oxides practically do not catalyze this reaction. In the presence of aluminum-molybdenum catalysts, the synthesis of thiophene can be accomplished only when 25% molybdenum oxide is present in them. Aluminum-chromium catalysts have high activity in this reaction. The introduction of lanthanum and potassium oxides results in a considerable increase in the reactivity and stability of the aluminum-chromium catalysts. The following conditions were selected as a result of the investigation: a reaction temperature of 560-580°, a space velocity of 220-280  $\text{h}^{-1}$ , molar ratios of  $\text{H}_2\text{S}$  and n- $\text{C}_4\text{H}_{10}$  from 2:1 to 2.5:1; a catalyst containing 1%  $\text{K}_2\text{O}$ , 5%  $\text{La}_2\text{O}_3$ , 5%  $\text{Cr}_2\text{O}_3$ , and 89%  $\text{Al}_2\text{O}_3$ , which has the greatest activity, was developed. The stability of this catalyst was investigated in the course of 10 h of continuous operation, and the yield of thiophene in the first 3 h was 37-40% and decreased to 23% in the next 7 h.

The catalyst activity was completely restored after 1, 2, and 3 h of operation on regeneration with air for the same length of time as an operating cycle. No increase in the catalyst activity was observed on prior treatment of it with hydrogen and hydrogen sulfide. When it was treated with n-butane, the yield of thiophene decreased from 40% to 25-30%. Thorough purification of the starting n-butane and hydrogen sulfide to remove  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$  did not affect the catalyst activity. The activity of aluminum-lanthanum-chromium-potassium catalysts in the synthesis of thiophene from hydrogen sulfide and n-butane is apparently not associated with the percentage of  $\text{Cr}^{6+}$  ions in them. Thus the catalyst activity was not raised as the percentage of hexavalent chromium in an aluminum-chromium catalyst was increased. The pentavalent chromium ion was detected by means of ESR spectra in an aluminum-lanthanum-chromium-potassium catalyst, and  $\text{Cr}^{3+}$  was detected after 1 h of operation. On the basis of these results, the authors propose that the active centers of chemisorption of hydrocarbons in an aluminum-lanthanum-chromium-potassium catalyst contain chromium ions with valences below six.

It has been shown by x-ray diffraction [46] that the introduction of potassium and lanthanum oxides into an aluminum-chromium catalyst does not introduce appreciable changes in the phase composition.

In an aluminum-lanthanum-chromium-potassium catalyst, chromium oxide [47] has polyfunctional properties, particularly dehydrogenating and cracking properties with respect to  $\text{C}_4$  hydrocarbons, and, in the presence of hydrogen sulfide, also has heterocyclization properties. The introduction of potassium and lanthanum oxides into an aluminum-chromium catalyst results in considerable intensification of its dehydrogenating and heterocyclization properties and in a decrease in its cracking functions.

The initial information on the catalytic preparation of thiophene by the reaction of hydrogen sulfide with butylene is primarily from the patent literature [19, 41, 48-52]. The formation of thiophene can be expressed by the equation



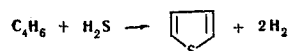
The catalysts recommended for this reaction are in most cases oxides or sulfides of group V-VIII metals, many of which are used on supports - aluminum oxide or silica gel. The experiments were carried out at 570-605° in excess (up to eightfold amounts) of hydrogen sulfide at atmospheric pressure in stationary and fluidized beds of catalyst. There is also information [52] that this reaction proceeds more effectively on dilution with inert gases such as nitrogen or carbon dioxide.

It should be noted that the yields of thiophene from butylene and hydrogen sulfide are, as a rule, considerably higher than from n-butane and hydrogen sulfide. As in the case of the reaction of hydrogen sulfide with n-butane, chromium-containing catalysts have the highest activity.

The literature data relative to the activity of an aluminum-chromium catalyst in the synthesis of thiophene from hydrogen sulfide and butylene are ambiguous [19, 25, 41, 51]. According to patent data [51], the maximum yield (69%) of thiophene from butylene and hydrogen sulfide is obtained in a fluidized bed of a catalyst containing SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and K<sub>2</sub>O.

An aluminum-lanthanum-chromium-potassium catalyst has high activity and greater stability than an aluminum-chromium catalyst in the synthesis of thiophene from hydrogen sulfide and butylene. When it was present, thiophene was obtained in a yield of approximately 52% [25-27, 29, 44, 45, 47].

The formation of thiophene from hydrogen sulfide and butadiene according to the equation



proceeds at lower temperatures than from n-butane and butylene [25, 29]. However, as a consequence of the higher reactivity of butadienes and n-butane or butylene, more side products are formed when it reacts with hydrogen sulfide. There is a patent [57] in which the positive effect of pressure (up to 30 atm) on the formation of thiophene from hydrogen sulfide and butadiene (the yield of thiophene increases from 22 to 63%) is demonstrated.

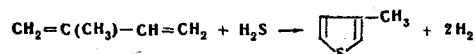
Chromium-containing catalysts also have considerable activity in this reaction. The yield of thiophene was 53% on an aluminum-lanthanum-chromium-potassium catalyst [25-27, 29, 41, 45, 47] at 500°, a H<sub>2</sub>S to C<sub>4</sub>H<sub>6</sub> ratio from 2:1 to 2.5:1, and a space velocity of 250-280 h<sup>-1</sup>. Thiophene was obtained in 50% yield on an aluminum-chromium-potassium catalyst [58, 63] at 400°, a feed space velocity of about 70 h<sup>-1</sup>, and a H<sub>2</sub>S to C<sub>4</sub>H<sub>6</sub> molar ratio of 2:1.

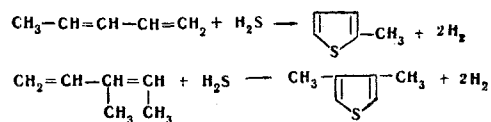
The equilibrium yields of thiophene [25, 29] at 427-627° and atmospheric pressure were determined as a result of a thermodynamic calculation of the interaction of hydrogen sulfide with n-butane, butylene, and 1,3-butadiene, and it was demonstrated that the yields obtained on active chromium-containing catalysts are 32-44% (or 60-90%, taking the side reactions into account) of the equilibrium values.

There are no data available with respect to the catalytic reaction of hydrogen sulfide with C<sub>5</sub>-C<sub>6</sub> paraffin hydrocarbons to form thiophene compounds. Until recently, there were only mentions [48, 55, 57] of a possible preparation of methylthiophenes by the reaction of hydrogen sulfide with 1-pentene, isoprene, or piperylene.

3-Methylthiophene was first obtained from hydrogen sulfide and isoprene in 25% yield on aluminum oxide containing iron oxide at 600°, a H<sub>2</sub>S and C<sub>5</sub>H<sub>8</sub> ratio from 4:1 to 8:1, and a contact time of 20 sec [54].

A detailed investigation of the catalytic synthesis of alkyl thiophenes from hydrogen sulfide and C<sub>5</sub>-C<sub>6</sub> diene hydrocarbons according to the equations





was carried out in the presence of chromium-containing catalysts. As a result, the following conditions were found: a reaction temperature of 470–500°, a space velocity of 0.5–0.7 h<sup>-1</sup>, a H<sub>2</sub>S–hydrocarbon molar ratio from 2 : 1 to 5 : 1, and a catalyst containing 4% K<sub>2</sub>O, 18% Cr<sub>2</sub>O<sub>3</sub>, and 78% Al<sub>2</sub>O<sub>3</sub>, on which 62, 75, and 59% yields, respectively, of 2- and 3-methylthiophenes and 3,4-dimethylthiophene were obtained from hydrogen sulfide and piperylene, isoprene, or 3,4-dimethyl-1,3-butadiene [59–66].

An aluminum–lanthanum–chromium–potassium catalyst (67%) [25–27, 44] and known industrial catalysts for the dehydrogenation of n-paraffin hydrocarbons (about 55%) [25–27] also have considerable activity in the synthesis of 3-methylthiophene from hydrogen sulfide and isoprene.

However, the stabilities of the chromium-containing catalysts indicated above in the synthesis of alkylthiophenes are low. The activity of a catalyst and its selectivity and stability are increased as a result of prior treatment with hydrogen. The average yield of 2-methylthiophene from piperylene and hydrogen sulfide after 80 operating cycles increases from 30% to 47% [63–66].

An examination of data on the synthesis of C<sub>5</sub>–C<sub>6</sub> alkylthiophenes from hydrogen sulfide and C<sub>5</sub>–C<sub>6</sub> diene hydrocarbons indicates that the yield of the target products depends only slightly on the structure of the starting hydrocarbon molecule and its degree of branching.

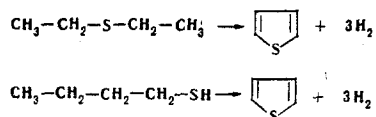
In addition to catalytic synthesis from hydrogen sulfide and individual hydrocarbons, thiophene and alkylthiophenes were also obtained from a mixture of C<sub>1</sub>–C<sub>6</sub> hydrocarbons in the presence of aluminum oxides [14]. In addition, these products were also obtained by the contacting of gases from the refining of lignite or gases from the cracking of Kuwait oil [52] with cobalt–molybdenum or vanadium catalysts. This as yet very limited experience with respect to the direct refining of hydrocarbon raw material without prior isolation of the individual hydrocarbons is particularly valuable from the point of view of a practical synthesis of thiophene and its homologs.

Encouraging preliminary results on the synthesis of thiophene were obtained using the butane–butylene fraction isolated in the Ufimskii Petroleum Refining Plant and freed of hydrogen sulfide, which was exhausted during hydropurification of the sulfurous oil [25].

A comparison of the data on the catalytic synthesis of thiophene from C<sub>4</sub> hydrocarbons and sulfur dioxide or hydrogen sulfide on oxide catalysts leads to the conclusion that it is apparently more expedient to obtain thiophene by the reaction of hydrocarbons with hydrogen sulfide. The following considerations are evidence in favor of this conclusion: the reaction of sulfur dioxide with hydrocarbons is accompanied by a considerable heat effect, which creates difficulties in the technological design of the process; the reaction forms not only thiophene but also water, carbon dioxide, and sulfur, while the gaseous products formed when hydrogen sulfide is used can be returned to the cycle. In addition, hydrogen sulfide is one of the components of the exhaust gases of the refining of sulfurous oils, while sulfur dioxide is obtained by the oxidation of sulfur or hydrogen sulfide.

### Preparation of Thiophene and Alkylthiophenes from Sulfur-Containing Organic Compounds

Dehydrocyclization of Aliphatic Sulfides and Mercaptans. The dehydrocyclization reactions of sulfur-containing compounds to thiophene proceed according to the equation



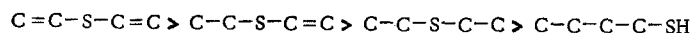
The formation of a thiophene ring from these compounds is thermodynamically possible at and above 227° [68, 69]. At 427°, the equilibrium is shifted almost completely to favor the formation of dehydrocyclization products. However, the equilibrium degree of cracking of a sulfur-containing compound at this temperature also reaches 100%. Kinetic factors therefore play an important role in dehydrocyclization reactions

[69]. An inert diluent [69] changes the ratio of the rates of these competitive reactions and promotes an increase in the yield of dehydrocyclization products. Thus the dehydrocyclization of organosulfur compounds to obtain thiophene is fraught with considerable difficulties.

The possibility of accomplishing this sort of reaction has been known for a long time. Meier [70] and Farager and co-workers [71] obtained thiophene and its homologs by passing aliphatic sulfides and disulfides through a red-hot tube. The formation of thiophene was later observed [72] from butyl mercaptan and di-n-butyl sulfide at 650-700° on silica gel. Thiophene was obtained at 300-500° in the presence of aluminum oxide from diethyl tetrasulfide or a suspension of sulfur in diethyl sulfide or ethyl mercaptan [73].

The catalytic transformations of aliphatic sulfides, primarily diethyl sulfide, were investigated in [68, 74-81] by the pulse method in the presence of catalysts containing group III and VI metals. It was shown that the principal directions of the catalytic transformations of diethyl sulfide at 250-600° are cracking reactions at the C-S bonds and dehydrocyclization to thiophene. Oxides and sulfides of chromium, titanium, vanadium, molybdenum, cobalt, tungsten, and rhenium catalyze the dehydrocyclization of diethyl sulfide, but the yields of thiophene do not exceed 13-15%. The activity of chromium-containing catalysts in these reactions depends on their chemical composition, which is determined by the nature of the support, by the presence of additives in the catalyst, and by the method used in the prior treatment of the catalyst. The most effective catalysts for the dehydrocyclization of diethyl sulfide are chromium oxide without a support and aluminum-chromium catalysts containing no less than 2.8% chromium. Chromium catalysts on such supports as silica gel and aluminum silicate are of low activity in this reaction. During the conversion of aliphatic sulfides, chromium oxide catalysts react with the hydrogen sulfide formed during cracking of the starting substance, as a result of which the catalyst contains a mixture of oxides and sulfides of chromium. By comparing the experimental data on the catalytic activity of samples in the conversion of diethyl sulfide with the changes in the ESR spectra of these catalysts, Mashkina and Sukhareva [80] concluded that the cracking of diethyl sulfide is accelerated by both sulfides and oxides of chromium, and that the latter are more active. However, the formation of thiophene from diethyl sulfide is catalyzed only by the sulfides of chromium. The authors emphasize that the regularities obtained are the same for the dehydrocyclization of dimethyl sulfide and the dehydrogenation of thiophene (see the section dealing with the dealkylation of alkyl thiophenes) and do not contradict the assumption of the presence of an overall limiting step in the formation of thiophene [81, 82].

The catalytic transformations of n-butyl mercaptan and a number of aliphatic C<sub>4</sub>, C<sub>6</sub>, and C<sub>8</sub> dialkyl sulfides, which differ in their structures and degree of unsaturation, were studied in detail in [69, 83-85]. The selection of the most effective catalysts for the dehydrocyclization of these compounds was made in the case of the conversion of diethyl sulfide at 350° and a space velocity of 0.9 h<sup>-1</sup>. A rhenium sulfide-alumina catalyst [86] and a catalyst containing 1.9% K<sub>2</sub>O, 0.8% CuO, 36.3% Cr<sub>2</sub>O<sub>3</sub>, and 61.0% Al<sub>2</sub>O<sub>3</sub> had the greatest activity in the formation of thiophene (the yield did not exceed 11%). The transformations of the organosulfur compounds indicated above in the presence of an aluminum-chromium-copper-potassium catalyst were studied in a flow system at 260-600° and space velocities of 0.25, 0.9, and 4.3 h<sup>-1</sup>. In the dehydrocyclization of diethyl, ethyl vinyl, and divinyl sulfides, as well as n-butyl mercaptan, the yield of thiophene increased both with an increase in the reaction temperature and on passing from a saturated organosulfur compound to an unsaturated compound [69]. The dehydrocyclization of n-butyl mercaptan to thiophene proceeds with particular difficulty. Thus, at 400° and a space velocity of 0.9 h<sup>-1</sup>, 32% thiophene was formed from divinyl sulfide, 20% thiophene was formed from ethyl vinyl sulfide, 7% thiophene was formed from diethyl sulfide, and only 5% thiophene was formed from n-butyl mercaptan. These compounds can be arranged in the following order with respect to their tendency to form thiophene:



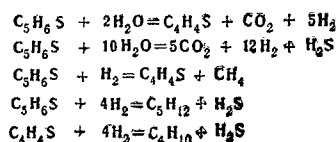
Conjugation of the free electron pair of the sulfur atom with the carbon-carbon double bond in unsaturated organosulfur compounds not only increases the tendency of the sulfide for dehydrocyclization but also results in strengthening of the C-S bond, which causes a relative decrease in the fraction of cracking products. However, this sort of conjugation is also responsible for the extreme tendency of these compounds for polymerization reactions.

Considerable amounts of various thiophene homologs - 2- and 3-methyl-, 2- and 3-ethyl-, 2,5- and 2,3-dimethylthiophenes - are formed along with thiophene and cracking products as a result of the catalytic transformations of n-butyl mercaptan and C<sub>4</sub> sulfides. Thus, at 400° and a space velocity of 0.9 h<sup>-1</sup>, 7%

alkylthiophenes were formed from divinyl sulfide, 5% alkylthiophenes were formed from ethyl vinyl sulfide, 4% alkylthiophenes were formed from diethyl sulfide, and 9.5% alkylthiophenes were formed from n-butyl mercaptan. Thiophenes (C<sub>8</sub>), including 2,5-diethylthiophene, were found in the catalyzate of the latter. Special experiments demonstrated that alkylthiophenes are not formed under the adopted catalysis conditions in the alkylation of thiophene by olefins or in the isomerization of any one thiophene. These substances are apparently obtained via different routes. In a study of the catalytic transformations of ethyl n-butyl and ethyl sec-butylsulfides, as well as di-n-propyl and diisopropyl sulfides, at 300-400° and a space velocity of 0.9 h<sup>-1</sup>, it was established that these compounds also undergo considerable cracking at the C-S bonds and, to a lesser degree, are dehydrocyclized to form alkylthiophenes. It was found that catalyzates of similar composition, which contain primarily 2- and 3-ethylthiophenes, as well as 2,4- and 2,5-dimethylthiophenes, result from the isomeric sulfides rather than the products of direct dehydrocyclization of the sulfides. The dehydrocyclization of isoalkyl sulfides proceeds more readily than that of normal alkyl sulfides. Thus the yield of 2,4- and 2,5-dimethylthiophenes from diisopropyl sulfide at 350° is 12% based on the catalyzate. These investigations indicate that the formation of thiophene compounds from dialkyl sulfide and n-butyl mercaptan proceeds via a complex route and is accompanied by diverse reactions.

Dealkylation of Alkylthiophenes. The demethylation of 2-methylthiophene to thiophene was first accomplished by Balandin and co-workers [87] using 50% Ni/Al<sub>2</sub>O<sub>3</sub>, 33% Ni/Al<sub>2</sub>O<sub>3</sub>, and 50% Co/Al<sub>2</sub>O<sub>3</sub> as catalysts under the influence of water vapors at 200-411° and H<sub>2</sub>O-C<sub>5</sub>H<sub>6</sub>S molar ratios from 27:1 to 170:1.

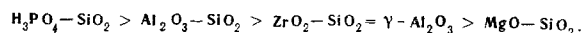
Up to 56% thiophene was detected in the liquid catalyzate in the first 4-6 min of the experiment at 250-334°. (The yield was not specified.) According to [87], the following reactions are involved in the process:



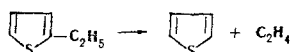
The authors assume that the formation of metal sulfides on the catalyst occurs under the influence of the hydrogen sulfide evolved. According to the data in a patent [88], thiophene can be obtained by the dealkylation or disproportionation of mono-, di-, and trimethylthiophenes in the presence of fluorinated aluminum oxide. At 550° and atmospheric pressure, 46.3% of a catalyzate, in which 36.9% thiophene, 8.5% dimethylthiophenes, and about 9% benzene and toluene were detected, was obtained from 2-methylthiophene in a stream of hydrogen (the H<sub>2</sub>-alkylthiophene ratio was 3:4, and the space velocity was 0.7 h<sup>-1</sup>) after 30 min. Similarly, 33.8% of a catalyzate containing 40.4% thiophene, 7.8% dimethylthiophenes, and 6.2% benzene and toluene, was obtained from 3-methylthiophene.

The dealkylation of methylthiophenes to thiophene and the effect of the acidity of the oxide catalysts on their activities in the transformations of 2- and 3-methylthiophenes were investigated in [89, 90]. The experiments were carried out in a flow-circulation apparatus at 250-600°. Thiophene, 3-methylthiophene, methane, hydrogen, hydrogen sulfide, and coke were detected in the products of the conversion of 2-methylthiophene.

It should be noted that thiophene and methylthiophene are thermally stable over the indicated temperature range in the absence of a catalyst. Samples of MgO, SiO<sub>2</sub>, and γ-Al<sub>2</sub>O<sub>3</sub> are active in the decomposition reaction, but they do not catalyze the demethylation and isomerization of 2-methylthiophene. The authors explain this by the fact that the Hammett acidity function of these catalysts is greater than three. The remaining catalysts were active in dealkylation and isomerization, and a linear dependence was observed between the acidity function and the logarithm of the rate constant referred to one equivalent of acid centers. The investigated catalysts can be arranged in the following order with respect to specific activity in demethylation and isomerization:



The formation of thiophene by the dealkylation of 2-ethylthiophene [90, 91]



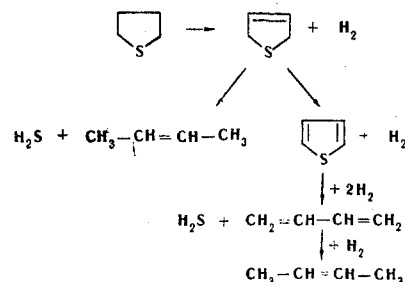
was observed under pulse conditions at 200–650° on catalysts of principally industrial preparation: aluminum–molybdenum, tungsten sulfide, iron–chromium–potassium, aluminum–chromium–potassium, calcium–nickel–phosphate, etc.

The dealkylation of 2-ethylthiophene in the presence of most of the catalysts investigated was accompanied by the formation of 2-vinylthiophene, and isomerization to 3-ethylthiophene also occurred on some of the catalysts.

Titanium dioxide, in the presence of which thiophene is obtained in a yield of 25%, has the greatest activity and selectivity in the dealkylation of 2-ethylthiophene at 280°.

It has been proposed [89–91] that the dealkylation of alkylthiophenes to thiophene proceeds at both protic and aprotic catalyst centers.

Dehydrogenation of Thiophane. The catalytic dehydrogenation of thiophane was first accomplished in 1936 by Yur'ev and Borisov [92]. The yields of thiophene reached 32% when thiophane was passed three times over a Pt/C catalyst at 400°. Thiophene was obtained in 18% yield in the presence of NiS/Al<sub>2</sub>O<sub>3</sub> at 350°. The authors proposed the formation of dihydrothiophene as an intermediate in the dehydrogenation of thiophane. The dehydrogenation of thiophane was complicated by the destructive cleavage of the heterocycles at the C–S bonds, as evidenced by the presence of H<sub>2</sub>S and butylene in the gaseous reaction products. The products of the conversion of thiophane are probably formed as a result of the following reactions:



A detailed investigation of the dehydrogenation of thiophane to thiophene was accomplished by Obolentsev and co-workers [93–95]. Their thermodynamic calculations indicate that this reaction is possible at atmospheric pressure at temperatures above 227°, and the equilibrium yield of thiophene is 100% at 427°. At 27–427°, the degree of dehydrogenation of thiophane decreases with increasing pressure and a decrease in dilution and is practically independent of these factors at 600–700°. The dehydrogenation of thiophane to thiophene was studied in [94] in a flow apparatus in the presence of industrial aluminum–molybdenum and aluminum–cobalt–molybdenum catalysts at atmospheric pressure, 300–500°, and an arbitrary contact time of 0.2–0.5 sec in benzene (an inert diluent). Thiophene was obtained in yields up to 75–78% at a space velocity of 0.2 sec<sup>-1</sup> and 454° on an aluminum–molybdenum catalyst and at 525° on an aluminum–cobalt–molybdenum catalyst. The K-5 catalyst at a space velocity of 0.5 sec<sup>-1</sup> and 550° showed somewhat lower activity: the yield of thiophene was 71% based on the amount of thiophane converted, for an overall degree of conversion of 96% [95]. However, after 6 h of operation of the catalyst, its activity decreased from 71% to 25%. Thiophane is also dehydrogenated to thiophene but less selectively (the yield is not specified) on a K-5 catalyst at 550° and a contact time of 0.5 sec in the absence of benzene.

The results of [96] on the dehydrogenation of the 180–190° and 190–200° fractions of monocyclic sulfides that were chromatographically isolated from the fractions of a concentrate of sulfurous compounds extracted from the kerosene distillate (150–250°) of Arlanskoilare interesting. The yield of thiophene decreased from 36.2% to 31% in the presence of an aluminum–chromium–molybdenum–potassium catalyst at 450°, atmospheric pressure, a space velocity of 2.0 h<sup>-1</sup>, and a H<sub>2</sub> to sulfide molar ratio of 1 : 4 after 500 h. An operating cycle was 45–60 min, and the time of regeneration of the catalyst with air was 2–3 h. The specified catalyst proved to be more active and selective in this process than a number of industrial catalysts (K-5, AP-56, aluminum–molybdenum, aluminum–cobalt–molybdenum, and aluminum–tungsten–nickel).

The dehydrogenation of thiophane to thiophene was accomplished on an aluminum–chromium–copper–potassium catalyst at 403° and a space velocity of 0.9 h<sup>-1</sup> [69, 83]. A total of 77% of a catalyzate, in which 48% thiophene and 52% thiophane were detected; was obtained. Only hydrogen and traces of methane were detected in the gas along with hydrogen sulfide. A study of the transformations of thiophane at 250–400° and

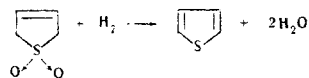


a space velocity of  $0.5-4 \text{ h}^{-1}$  on an industrial aluminum silicate catalyst demonstrated that dehydrogenation predominates at temperatures up to  $300^\circ$ , while decomposition of thiophane to hydrogen sulfide and olefins is the chief reaction above  $300^\circ$  [97, 98]. The maximum yield of thiophene was 14% based on the thiophane passed through the system. Poisoning of the aluminum silicate catalyst with  $\text{Na}^+$  ions from a  $\text{Na}_2\text{S}$  solution increases the selectivity of the catalyst in the formation of thiophene. Methyl ethyl sulfide, the percentage of which reached 50% of the converted thiophane on aluminum silicate and 35% on aluminum silicate treated with  $\text{Na}_2\text{S}$ , was detected along with thiophene and the starting thiophanes in the catalyzates. The authors assume that aliphatic sulfides and olefins are formed from the products of condensation via a polymerization-depolymerization mechanism.

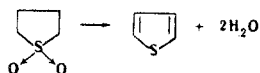
The transformations of thiophane were studied by the pulse method on oxides and sulfides of group III-VI metals [76, 81, 82]. Catalysts containing chromium on supports - VAU and AGN carbons, ZnO, MgO, and  $\gamma\text{-Al}_2\text{O}_3$  - proved to be the most active and selective catalysts for the dehydrogenation of thiophane to thiophene at  $250-600^\circ$ . The activities of the catalysts with respect to the dehydrogenation and cracking of thiophane vary antibatically and are caused by differences in the chemical compositions of the catalysts. Mashkina and Sukhareva [80] concluded that sulfides of chromium are an active component of chromium catalysts for the dehydrogenation of thiophane.

A comparison of the activity of chromium catalysts in the transformations of thiophane and diethyl sulfide demonstrated that cracking of diethyl sulfide at the C-S bonds proceeds at a greater rate than cracking of thiophane, but the orders of activities of the investigated catalysts practically converge with respect to the cracking of these compounds. The symbatic character of the catalytic activity is observed in the dehydrocyclization of diethyl sulfide and dehydrogenation of thiophane to thiophene, but the rate of formation of thiophene from thiophane is greater than from diethyl sulfide.

Hydrogenation and Dehydration of Sulfones. In 1948, Boyd [98] demonstrated the possibility of obtaining thiophene from sulfolene via the scheme



The reaction was carried out at  $250-600^\circ$  and 25-200 atm on Cu, Mo, and W oxides or sulfides. Thiophene can also be obtained from sulfolane. There are thermodynamic calculations [99] of various transformations of sulfolane, particularly its conversion to thiophene:



The formation of thiophene from sulfolane was studied in the presence of a number of industrial catalysts based on aluminum oxide containing Pt, Cr, Mo or Co-Mo. The reaction was accomplished at atmospheric pressure,  $300-500^\circ$ , and a raw-material feed rate of  $1-8 \text{ h}^{-1}$ , in an inert diluent (benzene). Thiophene formation was observed on all catalysts. The maximum yield of thiophene was obtained on a K-16 aluminum-chromium catalyst at  $400^\circ$ . The reaction was accompanied by the decomposition of the starting sulfolane to  $\text{SO}_2$  and  $\text{H}_2\text{S}$ ; mercaptans were not detected. In the absence of benzene, the yield of thiophene on K-16 catalyst was only 4.7%. Rhenium sulfide was later proposed [75] as the most effective catalyst for this reaction. It must be pointed out that sulfones are thermally unstable compounds. Thus sulfolane decomposes to butylene and  $\text{SO}_2$  at temperatures above  $300^\circ$ , while sulfolene decomposes to butadiene and  $\text{SO}_2$  at  $100^\circ$  [100]. \* At  $250-600^\circ$ , thiophene is actually therefore formed from butylene or butadiene and sulfur dioxide [98, 99].

## CONCLUSION

It follows from this review of the catalytic methods for obtaining thiophene and alkylthiophenes that the most expedient method will be one that is based on an accessible starting material, namely, hydrocarbons and hydrogen sulfide - products of the refining of sulfurous oils. This process may become extremely

\*Reference [100] missing in Russian original - Publisher.

promising in the case of the selection of active, stable, selective, and recoverable catalysts. The practical use of sulfur-containing organic compounds is hindered, since dialkyl sulfides, mercaptans, and thiophane are not yet being produced on a massive scale. The preparation of thiophene from sulfones is also unlikely, in connection with their unique properties, which are already finding application in the national economy.

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