

Catalytic Synthesis of Thiophene from Dialkyl Disulfides and *n*-Butane

A. Yu. Kopylov^a, R. R. Sadykov^a, K. G. Sadikov^a, A. M. Mazgarov^a, A. F. Vil'danov^a,
Z. R. Ismagilov^b, S. R. Khairulin^b, and S. A. Yashnik^b

^a Volga Research Institute of Hydrocarbon Feedstocks, ul. Ershova 35a, Kazan, 420045 Russia

^b Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences,
pr. Akademika Lavrent'eva 5, Novosibirsk, 630090 Russia

e-mail: vniius4lab@mail.ru

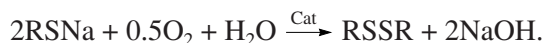
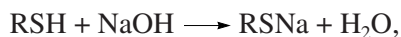
Received September 15, 2007

Abstract—A promising new method for thiophene synthesis on the basis of dialkyl disulfides (byproduct of demercaptanization of hydrocarbon feedstocks) catalyzed by a modified magnesia–chromia–alumina catalyst was developed.

DOI: 10.1134/S0965544108020060

A modern industrial process for hydrocarbon feedstock cleaning of mercaptans is their oxidation to dialkyl disulfides with molecular oxygen in an alkaline medium in the presence of phthalocyanine catalysts [1–4].

The following main reactions relevant to this treatment for the removal of mercaptans occur in the material:



As follows from this scheme, a byproduct of the process is a mixture of organic dialkyl disulfides RSSR, the so-called disulfide oil (DSO), a waste whose disposal from demercaptanization units is still an unresolved problem. To date, the disulfide oil has not found qualified application and is practically undisposable; meanwhile, its storage creates a safety hazard. Thus, the stock of DSO produced all over the world continuously grows. Therefore, the problem of the utilization of the disulfide oil via its processing into chemicals that are in demand is of great importance.

One of the possible ways of coping with the problem is the conversion of DSO into thiophene, a compound used for the synthesis of a range of valuable drugs for human and veterinary medicine, as well as chemicals for agriculture (herbicides and pesticides) [5–8]. New application areas of thiophene as a reactant for the fabrication of conducting and light-emitting polymers [9, 10], dyes and bleaching agents, additives for lubricating oils, and antiknocks [11, 12] are of great interest and perspective.

At present, according to [13–15], there are two main methods for the synthesis of thiophene and its derivatives: the catalytic reaction of C₄ oxygenates with

hydrogen sulfide or carbon disulfide in the presence of catalysts at moderate temperatures of 400–600°C. For preparative purposes, laboratory methods, in particular the Paal–Knorr synthesis, as well as the synthesis of thiophene from furan or pyrrole according to the Yur'ev reaction, can be used. The main drawbacks of these methods are the low economic efficiency, which is primarily due to the use of expensive and less available reagent materials, and an insufficient selectivity of the reactions. All of these factors result in a high production cost of the desired product thiophene.

In this work, we studied the feasibility of thiophene synthesis from organic dialkyl disulfides (disulfide oil) and *n*-butane using a modified magnesia–chromia–alumina catalyst.

EXPERIMENTAL

Feedstock components used in laboratory studies of thiophene synthesis were dimethyl disulfide containing a 99.57 wt % base substance; a mixture of organic dialkyl disulfides (disulfide oil) from the propane–butane demercaptanization unit (Orenburg gas processing plant) with dimethyl disulfide, methyl ethyl disulfide, and diethyl disulfide contents of 69.69, 24.54, and 3.15 wt %, respectively; and a grade B *n*-butane cut (TU (Technical Specifications) 0272-026-00151638-99) which contained 88.0 wt % *n*-butane (OAO Nizhnekamskneftekhim).

A special catalytic system containing chromium and magnesium oxides as an active component and potassium and/or lanthanum oxides as a promoter of the general formula $t\text{Mg}_{1-n}\text{Cu}_n\text{Cr}_2\text{O}_4-x\text{MgO}-y\text{K}_2\text{O}-z\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$, where t lies in the range 5 wt %; x , y , and z are at most 3.2, 2, and 10 wt %, respectively; and the value of n ranges within 0–1, was designed for the thiophene

synthesis from organic disulfides. The catalyst was prepared via the impregnation of a grained alumina support with a magnesium and/or copper dichromate solution of predetermined concentration and subsequent drying and thermal treatment. The impregnation was performed in the incipient wetness mode. In the final stage of treatment, catalyst grains containing magnesium and/or copper dichromate were promoted by admixtures of potassium and/or lanthanum oxides.

The process was conducted in a catalytic reactor with a fixed catalyst bed at a space velocity of 400–1800 h⁻¹, a temperature of 400–600°C, and an *n*-butane/dialkyl disulfide molar ratio in the range 1/(1–2).

The reaction mixture was analyzed chromatographically in the on-line mode with an LKhM-80 gas chromatograph equipped with a thermal conductivity detector, a 3000 × 3 mm column packed with 10% 1,2,3-tris-β-cyanoethoxypropane on diatomaceous earth, and a ATsP-E24 (L-Card) analog-to-digital converter; the data acquisition and processing program was NetChrom 2.1.

The yield of thiophene was determined according to the following formula in terms of *n*-butane fed:

$$Y = [C_{C_4H_4S}/C_{C_4H_{10}}]K \times 100\%,$$

where $C_{C_4H_4S}$ is the mass fraction of thiophene in the products (g/g), $C_{C_4H_{10}}$ is the mass fraction of *n*-butane in the reactants (g/g), and K is the ratio of the molar mass of thiophene to that of *n*-butane.

RESULTS AND DISCUSSION

Determination of the catalyst activity in the synthesis of thiophene is based on the study of the model reaction between *n*-butane and dimethyl disulfide (DMDS). This reaction is most complicated from the viewpoint of both its thermodynamic parameters and the mechanism of the process.

Earlier, Mashkina et al. [16–18] experimentally showed that, independent of the choice of the sulfur-containing feedstock, the activity of hydrogen sulfide-sulfided specimens of alumina–chromia catalysts during thiophene synthesis is somewhat higher than the activity of analogous oxide specimens. In this work, the catalyst was also sulfided; however, we used dimethyl disulfide as the sulfiding agent. This method significantly simplifies the sulfiding procedure, as dimethyl disulfide is less toxic than hydrogen sulfide and has a low vapor pressure, properties that facilitate its storage and accurate dosing. In addition, DMDS is a component of disulfide oil and is readily isolated upon its rectification, i.e., is a more available sulfiding agent.

Sulfidation was carried out according to the following procedures:

—sulfiding with pure DMDS in a helium flow at 450°C;

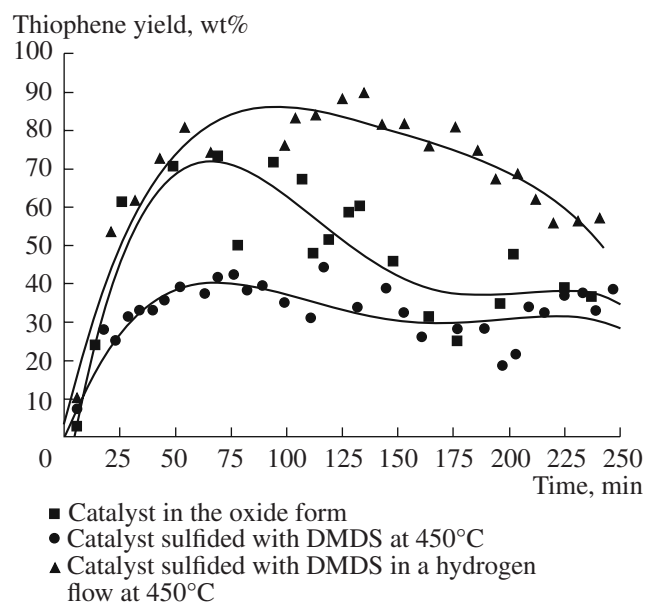


Fig. 1. Dependence of the magnesia–chromia–alumina catalyst activity in the synthesis of thiophene from dimethyl disulfide and *n*-butane on the sulfidation conditions: 580°C, the volume ratio of DMDS : *n*-butane = 1 : 1, contact time was 2 s (for Figs. 1–5, 7 and 8).

—sulfiding with DMDS in a hydrogen flow at a volume ratio of DMDS : H₂ = 1 : 3 and 450°C.

Figure 1 presents the data on the activity of catalysts in the oxide form and the catalysts sulfided according to these procedures. As follows from these data, the DMDS-sulfided catalyst shows the lowest activity: the yield of thiophene for 4 h was 40 wt %; the yield of thiophene on the catalyst in the oxide form for 2 h was 70 wt %; however, during the next 2 h, the yield rapidly decreased to 40 wt %. The highest activity and selectivity is exhibited by the catalyst sulfided with DMDS in a hydrogen flow; in this case, the yield of thiophene was 90 wt %.

This effect can be explained on the basis of published data [16–18]. As follows from that data, the activity of alumina–chromia catalysts in the synthesis of sulfur heterocycles strongly depends not only on the presence of sulfur in the catalyst, but also on the sulfur reactivity. The most active catalysts have sulfur bonded less strongly to the catalyst surface.

Thus, since one of the functional properties of the catalyst is dehydrogenation, active sites of the catalyst in the case of sulfidation with pure DMDS become partially coked because of the lack of hydrogen, owing to the complete dehydrogenation of hydrocarbon fragments formed during the thermal decomposition of DMDS. As a result of this unfavorable effect, a part of the catalyst surface is blocked with coke, thereby leading to a decrease in the catalyst surface area covered with active sulfur.

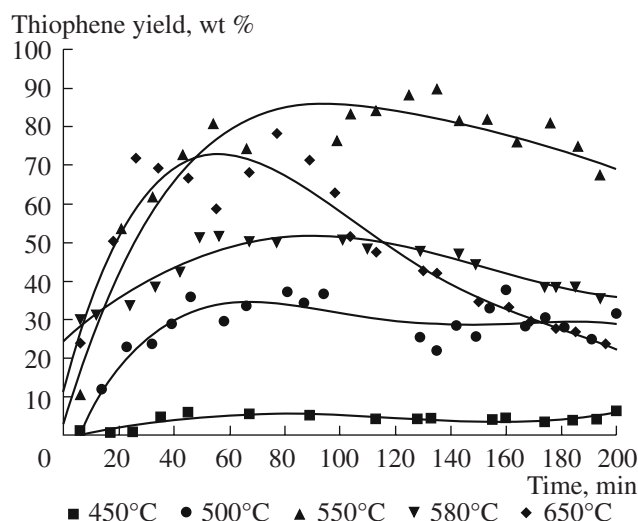


Fig. 2. Influence of temperature on the yield of thiophene from *n*-butane and DMDS; the DMDS : *n*-butane volume ratio is 1 : 1, the reactant concentration in helium is 10 vol %.

The same effect, although to a lower degree, is characteristic of the catalyst in the oxide form. It is likely that the oxide catalyst, exhibiting a higher cracking activity, decomposes the reactants at the initial stage of the process and the forming hydrogen sulfide converts metal oxides to the corresponding sulfides, which are active in the cyclization reaction; however, a portion of the active centers become coked as a result of the parallel reaction of *n*-butane dehydrogenation.

These negative factors can be minimized by the sulfiding catalyst with DMDS in a hydrogen stream.

An analysis of the data presented in Fig. 1 leads to the conclusion that the choice of the sulfiding agent and the sulfidation procedure are important aspects in the synthesis of thiophene from dialkyl disulfides and *n*-butane. Thus, the preliminary sulfidation of the catalyst with DMDS in a hydrogen flow at 450°C significantly improves the catalyst performance characteristics: conversion, selectivity, and stability of operation. Therefore, the following experiments were conducted using the catalyst sulfided with DMDS in a hydrogen flow.

The next step of the work was to determine the influence of the reaction temperature on the catalyst activity, which was evaluated as the yield of thiophene.

A characteristic property of dialkyl disulfides is the relatively low strength of their S–S and C–S bonds, which break upon heating or the interaction of dialkyl disulfides with the catalyst surface. Thermodynamically, the formation of thiophene from DMDS and *n*-butane is allowed even at 300°C. However, as follows from the experimental data (Fig. 2) on varying the temperature in the range 300–650°C, the formation of thiophene takes place only at temperatures above 450°C. In noticeable amounts (more than 50 wt %), thiophene is formed beginning from 550°C and reaches

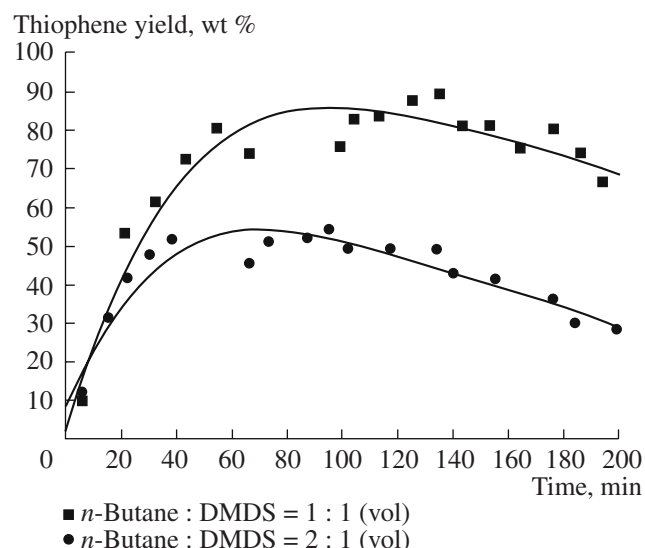


Fig. 3. Dependence of the thiophene yield on the ratio of *n*-butane to DMDS at 580°C and a reactant concentration in helium of 10 vol %.

its maximum yield of 90 wt % at 580°C. The elevation of the temperature above 600°C does not produce a favorable effect: on the contrary, the catalyst is quickly deactivated and its activity falls from 70 to 40 wt % within 2 h. The rapid deactivation of the catalyst at temperatures above 600°C is associated with its coking due to the acceleration of the dehydrogenation reaction.

As follows from the data given in Fig. 3, an increase in the *n*-butane-to-DMDS ratio from equimolar to two-fold excess decreases practically twice the yield of thiophene on a fed *n*-butane basis. Thus, the increase in the hydrocarbon-to-dialkyl disulfide ratio gives no positive effect.

An increase in the concentration of the reactants DMDS and *n*-butane in helium from 10 to 30 vol % (Fig. 4) significantly decreases the thiophene yield from 90 to 50 wt %. This decline can be explained by the fact that the fixed-bed mode of catalyst operation cannot ensure the ideal displacement conditions and, thus, makes it impossible to attain the maximal catalyst productivity. In the stationary regime, even small deviations of the ratio of the reactor diameter to the catalyst grain diameter leads to the disturbance of the plug flow; as a result, the local linear gas velocity can significantly deviate from the average value. The use of an ebullating bed of the catalyst can prevent negative phenomena, such as the breakthrough and the formation of dead spaces; decreases the degree of catalyst coking; and increases its activity in comparison with the fixed bed.

Taking into account the results of investigations concerning the influence of the main parameters (temperature, concentration, and reactant ratio) on the catalytic activity, we conducted three-cycle experiments on thiophene synthesis from *n*-butane and DMDS (Fig. 5);

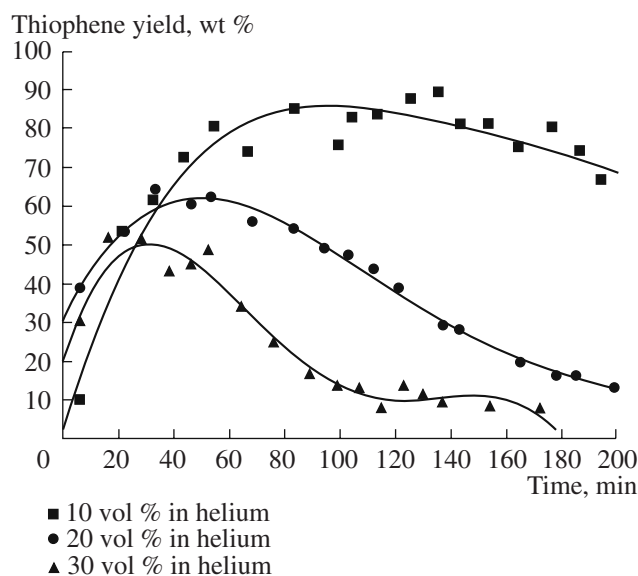


Fig. 4. Dependence of the thiophene yield on the concentration of *n*-butane and DMDS in helium at 580°C and a DMDS : *n*-butane volume ratio of 1 : 1.

each cycle included three stages: sulfidation–synthesis–regeneration.

As follows from the results of the study of the model reaction of thiophene synthesis from dimethyl disulfide and *n*-butane, the magnesia–chromia–alumina catalyst makes it possible to maintain the thiophene yield at a level of 60–90 wt % during 4 h; afterwards, the yield of thiophene gradually decreases (up to 30–40 wt %). To recover the catalytic activity, the catalyst was subjected to oxidative regeneration with air oxygen at 580°C. It was found that the carbon is removed as carbon dioxide from the deactivated catalyst surface. The higher the initial amount of carbon in the specimen, the longer the full catalyst regeneration time. The regeneration conditions employed, ensuring the removal of coke from the catalyst surface, leave intact both the phase composition of the catalyst and the electronic state of chromium.

It follows from the analysis of the results obtained in the second and the third cycle that the catalyst almost completely recovers its catalytic properties after regeneration.

The aim of the kinetic experiments was to obtain an accurate mathematical description of the model reaction on the basis of the experimental data. Studying the kinetic behavior of the reaction of the thiophene synthesis from DMDS and *n*-butane on a magnesia–chromia–alumina catalyst showed that the reaction is first order in dimethyl disulfide at the initial period of time.

Based on the analysis of the results of the experiments, we obtained the rate equation: $w_{\text{DMDS}} = -dC_{\text{DMDS}}/d\tau = k_0 \exp(-E_A/RT)C_{\text{DMDS}}$.

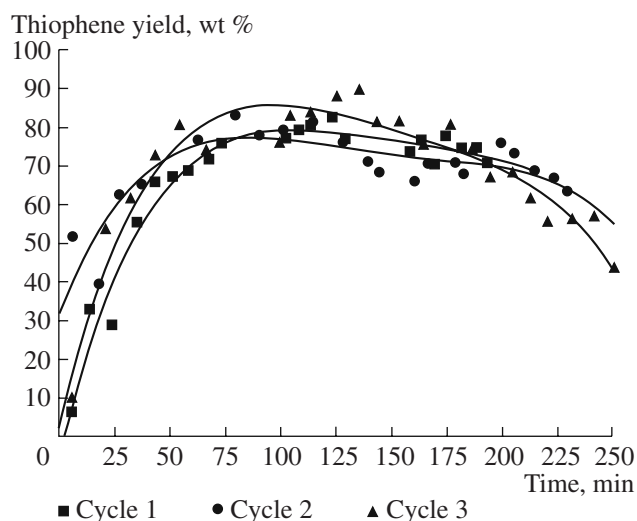


Fig. 5. The yield of thiophene during its synthesis from *n*-butane and DMDS: reactant concentration of the reactants in helium was 10 vol %, temperature was 580°C, and DMDS : *n*-butane = 1 : 1 (vol).

The parameters of the rate equation are as follows: $K_0 = 0.084 \text{ min}^{-1}$ and the activation energy E_A of the process in the temperature range 550–580°C is 2295 J/mol at the initial period of time.

The calculated and experimental data for the model reaction of thiophene synthesis are collated in Fig. 6.

As follows from the obtained data, the proposed kinetic model is not universal; in our case, this model adequately describes the region at the initial period of the reaction at temperatures in the range 550–580°C. This fact allows us to assume that thiophene is initially formed from DMDS at the optimal temperature of 580°C and, then, its formation follows a complex multistage mechanism that cannot be described by this simplified kinetic model.

An analysis of the composition and concentration of the components of the reaction mixture (Fig. 7) in the synthesis of thiophene from *n*-butane and DMDS showed that the equilibrium mixture predominantly consists of methane, thiophene, and hydrogen sulfide. There were no reaction products other than these. The obtained experimental data agree with the results of a preliminary calculation of the equilibrium composition of a gaseous mixture for the reaction between *n*-butane and dimethyl disulfide with the use of the IVTANTERMO program, which makes it possible to calculate the equilibrium parameters of gaseous mixtures on the basis of the thermodynamic data.

The results obtained in this work confirm the stepwise mechanism of the thiophene formation suggested previously [16–18]. At the first stage, the interaction of dimethyl disulfide with the surface of a sulfided catalyst leads to the dissociative absorption of the disulfide with the cleavage of the S–S and C–S bonds and the forma-

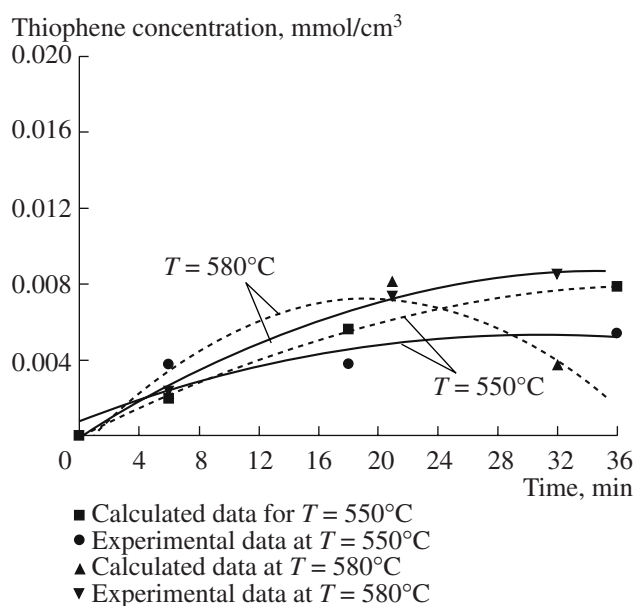


Fig. 6. Experimental and calculated rate curves for thiophene formation at 550°C and 580°C.

tion of adsorbed hydrocarbon fragments that undergo further transformations (dimerization, dehydrogenation, etc.) on the catalyst surface under the given conditions:

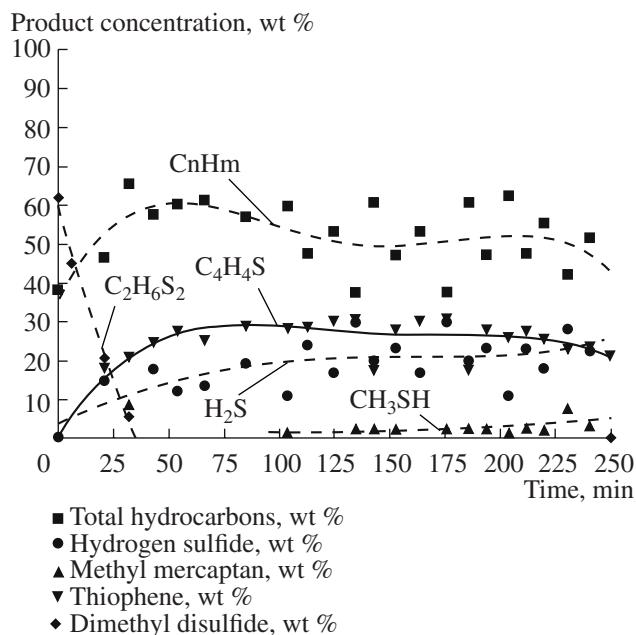
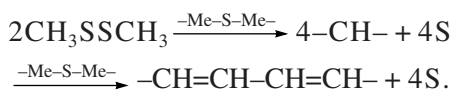
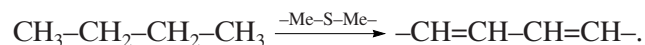


Fig. 7. Product concentrations during the course of thiophene synthesis from *n*-butane and DMDS at 580°C and DMDS : *n*-butane = 1 : 1 (vol).

Along with the dissociative adsorption of dimethyl disulfide on the catalyst surface, *n*-butane undergoes dehydrogenation yielding the reactive hydrocarbon fragment:



Condensation of these dehydrogenated hydrocarbon groups with the surface sulfur of the catalyst results in the formation of the thiophene ring:



Being desorbed from the catalyst surface, the thiophene takes away a portion of the sulfur, thereby resulting in catalyst deactivation. The next stage is the resulfurization of the catalyst surface by the reaction medium: $\text{Cat}[\] + \text{S} \rightarrow \text{Cat}[\text{S}]$.

It also follows from the obtained data that the decline in the catalyst activity is due to the deactivation of the catalytic active sites responsible for the cyclization of the thiophene ring because of an increase in the carbon load on the catalyst active sites. The increase in the methyl mercaptan and hydrogen sulfide concentrations in the equilibrium mixture is a clear indication of this fact.

The results presented in Fig. 8 show that, in the case of the disulfide oil used instead of dimethyl disulfide, the magnesia–chromia–alumina catalyst maintains the yield of thiophene at a level of 60–100 wt % for 2 h; afterwards, the yield of thiophene decreases (up to 30–40 wt %). This finding can be explained on the basis of the assumption that an increase in the proportion of disulfides with a higher molecular mass in the feed mix-

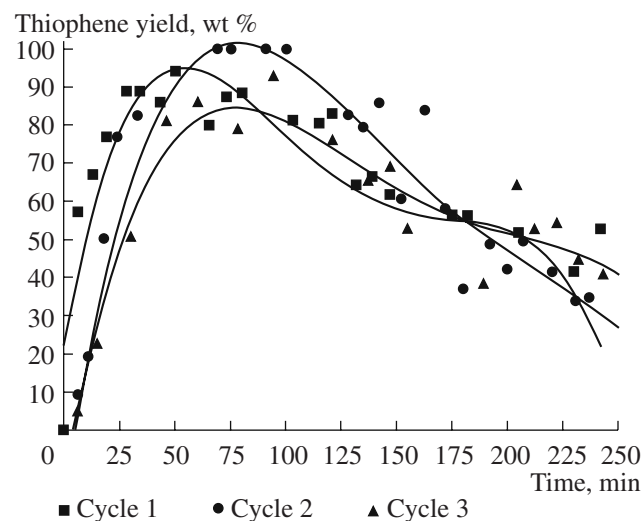


Fig. 8. The yield of thiophene during its synthesis from *n*-butane and disulfide oil at 580°C at a concentration of reactants in helium of 10 vol % and a disulfide oil : *n*-butane volume ratio of 1 : 1.

ture (methyl ethyl disulfide, diethyl disulfide, etc.) facilitates their decomposition to the corresponding mercaptans followed by the transformation of the latter to thiophene.

To summarize, it was shown that aliphatic disulfides or their mixtures can be used for the catalytic synthesis of thiophene. The process proceeds in the presence of a magnesia–chromia–alumina catalyst modified with potassium and lanthanum oxides, with the yield of thiophene depending on the length of the alkyl radicals in the reactant dialkyl disulfide and on the reaction conditions. The developed method makes it possible to obtain thiophene with a yield of up to 90 wt % under appropriate conditions.

Further investigation into the synthesis of thiophene from the disulfide oil will be conducted using the ebullating bed of the catalyst, an arrangement that will presumably increase the lifetime and the activity of the catalyst.

REFERENCES

1. P. Urban, US Patent No. 3,260,665 (1967).
2. S. Takase, M. Nambu, et al., US Patent No. 3,565,959 (1971).
3. S. A. Borisenkova, A. F. Vil'danov, and A. M. Mazgarov, *Russ. Khim. Zh.* **39** (5), 87 (1995).
4. A. F. Vil'danov, A. I. Lugovskoi, A. M. Mazgarov, et al., *Neftepererab. Neftekhim.*, No. 7, 15 (1991).
5. H. D. Hartough, *Thiophene and Its Derivatives* (Wiley, New York, 1952).
6. L. I. Belen'kii, E. P. Zakharov, and M. A. Kalik, *New Trends in Thiophene Chemistry* (Nauka, Moscow, 1976) [in Russian].
7. N. T. Bikbulatov, in *Chemistry of Organic Sulfur Compounds in Petroleum and Petroleum Products* (Vysshaya Shkola, Moscow, 1972), Vol. 9, p. 67.
8. I. M. Nasyrov and I. U. Numanov, in *Proceedings of III Republican Scientific and Technical Conference on Petroleum Chemistry, Gur'ev, 1977*, No. 9, p. 2152.
9. <http://www.azom.com>.
10. <http://www.netcomposites.com>.
11. M. G. Voronkov, E. N. Deryagina, N. A. Korchevin, et al., RU Patent No. 2 036 920 (1995).
12. M. G. Voronkov, E. N. Deryagina, N. A. Korchevin, et al., RU Patent No. 2 063 967 (1996).
13. B. W. Southward, G. J. Hutchings, and R. W. Joyner, *Catal. Lett.* **68**, 75.
14. Barrault, et al., US Patent No. 4,143,052 (1978).
15. Clark, et al., GB Patent No. 1,345,203 (1974).
16. T. S. Sukhareva, L. V. Shepel', and A. V. Mashkina, *Catalysts of Processes of Synthesis and Transformations of Sulfur Compounds* (Novosibirsk, 1979) [in Russian].
17. T. S. Sukhareva, L. V. Shepel', and A. V. Mashkina, *Kinet. Katal.* **19**, 654 (1979).
18. A. V. Mashkina, *Heterogeneous Catalysis in Chemistry of Sulfur Organic Compounds* (Nauka, Novosibirsk, 1977) [in Russian].