# Reaction of Dimethyl Disulfide with Thiophene Catalyzed by Zeolite

A. V. Mashkina and L. N. Khairulina

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, pr. Akademika Lavrent'eva 5, Novosibirsk, 630090 Russia e-mail: amash@catalysis.ru

#### Received June 6, 2014

**Abstract**—Reaction of dimethyl disulfide with thiophene under the action of highly siliceous zeolite at 180–350°C and contact time 0.6–14 s resulted in formation of thioalkylation products, 2-(methylsulfanyl)- and 2,5-bis(methylsulfanyl)thiophenes and also alkylated derivatives, 2-methyl-, 2,5-dimethyl-, and 2,3,4-trimethyl-thiophenes.

## DOI: 10.1134/S1070428015020141

(Alkylsulfanyl)thiophenes<sup>\*</sup> may be used as additives to lubricating oils and polymers to improve their thermooxidative stability, in the synthesis of herbicides and electroconducting materials [1]. One of the procedures for the preparation of (alkylsulfanyl) thiophenes is the reaction of dialkyl disulfides with thiophene. In [2–4] the reaction of dimethyl disulfide with thiophene was investigated catalyzed with zinc or manganese chlorides applied on the montmorillonite support. In chlorobenzene (80-150°C, 8-48 h, molar ratio disulfide-thiophene 8 : 1) in argon the thiophene conversion was 35-50%, and 2,3,4-, 2,3,5-tris-(methylsulfanyl)thiophenes and 1,2,3,4-tetrakis-(methylsulfanyl)thiophene were obtained. The reaction carried out at pressure and when adding some air to argon (150°C, 5 h) along with tri-and tetra-substituted thiophenes provided also a small quantity of 2,5-bis-(methylsulfanyl)thiophene.

In this study in order to obtain mainly mono- and bis(methylsulfanyl)thiophenes the reaction between dimethyl disulfide and thiophene was carried out in the presence of highly siliceous zeolite HZSM-5. On the surface of this catalyst a large number of strong proton sites is present, and also strong Lewis acid centers and basic sites of a moderate strength [5]. The mentioned sites may activate the reagents. Contacting with the zeolite, like in the acid solution, thiophene is protonated with the formation of a thiophenium ion [6, 7]. Dimethyl disulfide is coordinated with the acid and basic sites of the zeolite leading to the rupture of the S–S and C–S bonds and to the formation of  $CH_3S$  and  $CH_3$  fragments undergoing further transformations [8]. It was expectable that in the reaction of dimethyl disulfide with thiophene zeolite HZSM-5 would exhibit a high catalytic activity which would result in of the polysubstituted thiophene derivatives.

We investigated the reaction of dimethyl disulfide with thiophene in helium atmosphere and at normal pressure varying the temperature (180–350°C), the contact time, and the molar ratio of reagents.

We carried out separate experiments with individual dimethyldisulfide and thiophene (180-350°C, contact time 0.7-3.6 s, initial concentration of dimethyl disulfide 4-5 vol %, of thiophene, 1.4-1.6 vol %). Dimethyl disulfide under these conditions readily decomposed giving methanethiol, dimethyl sulfide, hydrogen sulfide, dimethyl tri- and -tetrasulfides, carbon disulfide, and ethylene. The increase in the temperature and contact time resulted in growing conversion of the dimethyl disulfide; the yields of dimethyl tri- and -tetrasulfides decreased, and of the other products, increased. Some decomposition of thiophene was observed only at the temperature over  $300^{\circ}$ C: its conversion was 3–10%, hydrocarbons C<sub>1</sub>–C<sub>2</sub> formed in 1.5-4.0 mol % yield, the obtained high boiling compounds were not identified.

The experiments on conversion of the mixture of dimethyl disulfide with thiophene were carried out at

<sup>\*</sup> Formerly named (alkylthio)thiophenes.

180–350°C, contact time 0.6–14 s, molar ratio disulfide–thiophene 2–7.8 : 1. Under these conditions thioalkylation products were obtained: 2-(methylsulfanyl)thiophene and 2,5-bis(methylsulfanyl)thiophene, and also alkylation products: 2-methylthiophene, 2,5-dimethylthiophene, and 2,3,4-trimethylthiophene, not found previously in [2–4]. Dimethyl disulfide unreacted with thiophene trans-formed in the same products as at the decomposition of the individual disulfide.

The conversion of dimethyl disulfide in the mixture with thiophene at a relatively low temperature was considerably smaller then the conversion of dimethyl disulfide without thiophene; the conversion grew with the growing temperature For instance, at the contact time 1.2 s and the molar ratio disulfide–thiophene 4–5 : 1 the conversion of dimethyl disulfide was as follows, %:

350
92
90

The yields of methanethiol, dimethyl sulfide, and hydrogen sulfide in the runs with the mixture of

dimethyl disulfide with thiophene were somewhat lower than at the decomposition of individual dimethyl disulfide. The decrease in the conversion and the yields of products originates from the reduced active surface of the catalyst where a part of the sites is occupied by the chemosorbed thiophene.

The thiophene conversion in the runs with the mixture with dimethyl disulfide grew with the growing temperature. For instance, at the contact time 2.3-2.5 s and the molar ratio of the reagents 4-5: 1 at the temperature 180, 200, 250, 300, and 350°C the conversion reached 14, 16, 22, 31, and 43% respectively.

The yield of thiophene derivative depended on the reaction conditions, some results are compiled in the table. At increasing molar ratio dimethyl disulfide–thiophene the conversion of thiophene and the products yields somewhat grew. In various conditions the yield of 2-(methylsulfanyl)thiophene was  $\sim 1.5$ –3 times higher that the yield of 2,5-bis(methylsulfanyl) derivative. The yields of mono- and trimethylthiophenes were close, and the yield of 2,5-dimethylthiophene was significantly lower. The overall yield of the

Contact time, s	Thiophene conversion, %	Yield, mol %					
		Thioalkylation products		Alkylation products			
		2-(methylsulfanyl)-	2,5-bis(methyl-	2-methyl-	2,5-dimethyl-	2,3,4-trimethyl-	
		thiophene	sulfanyl)thiophene	thiophene	thiophene	thiophene	
Temperature 180°C							
1.2	7	3.2	2.0	0.3	0.1	1.5	
2.3	14	5.3	4.5	1.7	0.3	2.2	
4.9	19	7.1	5.0	3.3	0.7	3.0	
5.0 <sup>a</sup>	17	7.7	3.7	2.7	0.7	2.0	
4.9 <sup>b</sup>	26	9.2	5.5	4.8	2.2	4.0	
8.8	28	10.4	7.1	4.4	0.6	3.8	
14.0	42	17	11.0	6.0	1.8	5.0	
Temperature 300°C							
0.6	14	1.3	0.7	7	1.5	4.5	
1.2	24	2.0	1.0	10	2.0	9.0	
1.2 <sup>a</sup>	20	2.1	2.5	8	1.4	5.3	
1.2 <sup>b</sup>	35	4.2	3.4	14	3.0	10	
2.3	31	1.6	0.5	13	6.0	10	
4.9	42	1.3	0.4	16	9.0	12	
8.5	51	1.1	0.2	19	12	18	

**Table.** Effect of conditions on thiophene conversion and yields of products of thioalkylation and alkylation. Catalyst HZSM-5, molar ratio dimethyl disulfide-thiophene, 4–5 : 1

Molar ratio dimethyl disulfide-thiophene: <sup>a</sup> 2.0–2.2, <sup>b</sup> 7.4–7.8.



thioalkylation products at the relatively low temperature exceeded the yield of the alkylation products. At high temperature the yield of the thioalkylation products was low, mainly the alkylsubstituted thiophenes were obtained (see the scheme).

The process results were affected by the contact time. At the constant temperature and reagents concentration the thiophene conversion grew with the contact time. At the low temperature with the growing contact time both yields of thioalkylation and alkylation products of thiophene increased. At the high temperature the thioalkylation products formed in a low yield, and it decreased with the growing contact time, and the yields of the thiophene alkylation products increased, but insignificantly. At various temperatures the overall selectivity of thiophene derivatives formation at varying the thiophene conversion was approximately constant (see the figure).

This suggests that the reactions proceed by two independent routes.

The maximum selectivity of (methylsulfanyl)thiophenes formation was attained at the temperature below 200°C and was ~70%, at higher temperature it decreased. This was due to decomposition of CH<sub>3</sub>S fragments at raising the temperature [9–11]. The arising increased amount of CH<sub>3</sub> fragments results in the growing formation of methylthiophenes whose overall formation selectivity attains 90%.



Selectivity of formation of products of thioalkylation (1, 2) and alkylation (3, 4) at various thiophene conversions.

## EXPERIMENTAL

We used as catalyst an industrial sample of highly siliceous zeolite HZSM-5 in a hydrogen form (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 34) ( $S_{sp}$  500 m<sup>2</sup>/g) calcined before use in a stream of dry air for 5 h at 530°C. The substances used in the study were reagents of "pure" grade.

The catalysis experiments were carried out at atmospheric pressure in a flow reactor with a fixed catalyst bed, catalyst grains of 0.25-0.5 mm, under conditions excluding diffusion difficulties. Each run was performed with the use of fresh catalyst. The system was totally under temperature control. Into the saturators filled with dimethyl disulfide and thiophene placed in thermostats helium was passed from a gas cylinder. After mixing the gas saturated with dimethyl disulfide and thiophene was passed into the reactor with catalyst heated at the desired temperature. The gas sampling was carried out every 45 min within ~2 h. The high boiling products were condensed in a cooled receiver.

Reaction products were identified by GC-MS on an instrument Agilent 7000 GC/MS Triple Quad equipped with a capillary column (30 m  $\times$  0.25 mm), stationary phase HP-5MS. The quantitative analysis was carried out on a chromatograph LKhM-8MD equipped with a katharometer, column 2 m  $\times$  3 mm, stationary phase XE-60 on Chromaton AW-LMCS, carrier gas helium. Contact time is equal to the ratio of the catalyst volume  $(cm^3)$  to the gas flow rate  $(cm^3/s)$ at room temperature and atmospheric pressure. The conversion of thiophene and dimethyl disulfide, and also the yields of the reaction products were calculated from the concentration of the formed product with respect to the initial concentration of the substarte (mol %), and the selectivity of product formation was evaluated from the ratio of its yield to the substrate conversion.

## REFERENCES

1. Stoyanovich, F.M., *Novye napravleniya khimii tiofena* (New Trends in the Chemistry of Thiophene), Gol'dfarb, F.M., Ed., Moscow: Nauka, 1976.

- 2. Clark, P.D., Mesher, S.T.E., and Primak, A., *Phospho-rus, Sulfur, Silicon Relat. Elem.*, 1996, vol. 114, p. 99.
- Clark, P.D., Mesher, S.T.E., Primak, A., and Yao, H., *Phos-phorus, Sulfur, Silicon Relat. Elem.*, 1997, vol. 120, p. 413.
- 4. Clark, P.D., Mesher, S.T.E., Primak, A., and Yao, H., *Catal. Lett.*, 1997, vol. 48, p. 79.
- Mashkina, A.V., Chem. Sustain. Develop., 2012, vol. 20, p. 181.
- Belen'kii, L.I., *Chem. Heterocycl. Comp.*, 1992, vol. 28, p. 610.
- Chica, A., Strohmaer, K.G., and Iglesia, E., *Langmuir*, 2004, vol. 20, p. 10982.
- 8. Mashkina, A.V., *Kinet. Catal.*, 2008, vol. 49, p. 802.
- Kang, D.H. and Friend, C.M., *Langmuir*, 2004, vol. 20, p. 1144.
- Halevi, B. and Vohs, J.M., J. Phys. Chem. B, 2005, vol. 109, p. 23976.
- 11. Huang, T.P., Teng, T.F., and Hung, W.H., Surf. Sci., 2009, vol. 603, p. 1244.