

# SYNTHESIS OF PREMIUM MOTOR FUEL FROM MIDDLE DISTILLATES WITH HIGH CONTENT OF THIOPHENE AND DIBENZOTHIOPHENE.

D. G. Aksenov, O. V. Klimov and G. V. Echevsky

Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Ak. Lavrentieva Avenue 5, 630090, Novosibirsk, Russia, e-mail: D.G.Aksenov@catalysis.nsk.su

**Abstract.** Conversion of oil distillate (cut points 30-360°C; Verkh-Tarsk oil field) with added extra amount of thiophene and dibenzothiophene was studied under the BIMF process conditions. It is found that the catalyst deactivation increases with the thiophene concentration growth in the feed, probably owing to the active sites blocking by thiophene conversion products. Usage of new type of catalyst together with circulation of the gaseous reaction products results in full absence of thiophene and dibenzothiophene in the produced motor fuel.

**Key words:** motor fuel production, thiophene and dibenzothiophene transformation, zeolite catalyst.

## Introduction

Manufacture of non-polluting high-quality motor fuels is one of the actual and priority tasks of oil refining. Boreskov Institute of Catalysis has developed a new technology – BIMF (Boreskov Institute Motor Fuels BIMF) of one-stage conversion of oil distillates with boiling points up to 360°C or gas condensates to high octane gasoline, diesel fuel (winter grade) and liquified gases C<sub>3</sub>-C<sub>4</sub> [1,2]. This technology allows substantial lower of power consumption in motor fuels manufacturing. The process is carried out over a zeolite catalyst not containing noble metals in a temperature range 350-450°C. Gasoline produced at the given conditions contains less than 35 wt. % of aromatic compounds, up to 10 wt. % n-alkanes, the rest being i-alkanes and naphthenes. Diesel fuel consists mainly of i-alkanes and naphthenes, the content of n-alkanes does not exceed 5 wt. %, the content of aromatic compounds is less than 10 wt. %.

At these conditions the transformation of oil distillates which do not contain the most stable thiophene or its derivatives results in the residual sulfur content in the produced gasoline less than 0.01 wt. %, in diesel fuel less than 0.05 wt. %. On the other hand, it is commonly known that one of the main problems of oil refining is a removal of thiophene and its derivatives from motor fuels. In this connection, in the present work we investigate an influence of thiophene and dibenzothiophene concentration in raw materials on both activity and stability of the catalyst in conditions of carrying out the BIMF process. The mechanism of conversion of sulfur containing compounds over various catalysts is proposed.

## Experimental

In the present work we have used a commercial catalyst IC-30-BIMF containing ZSM-5 zeolite with molar ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 80 (M1). Other catalysts have been prepared by me-

chanical mixture of the initial IC-30-BIMF with HDS catalysts: commercial catalyst GO-70 (M2) and high active laboratory samples Ni-Mo/Al<sub>2</sub>O<sub>3</sub> (M3) and Co-Mo/Al<sub>2</sub>O<sub>3</sub> (M4) which has been prepared by anchoring of Mo<sup>5+</sup> oxalate complexes on a surface of alumina [3].

Oil distillate (cut points 30-360°C) from Verh-Tarsk oil field (Novosibirsk region, Russia) with the total content of sulfur less than 0.5 wt. % was used as a feedstock. The distillate has the following group composition (% wt.): dissolved gas – 1.2, gasoline fraction – 63.5 and diesel fraction – 35.3. The content of n-alkanes in the distillate is – 31.2 %, aromatic compounds – 7.3 % the rest being naphthenes and i-alkanes. Starting with this raw material several model mixtures with thiophene content of 1.2 % wt., 2.2 % wt., 3.5 % wt. and the dibenzothiophene concentration of 3.5 % wt. as well as the mixture containing 3.5 % wt. of thiophene and 2.5 % wt. of dibenzothiophene have been prepared.

Transformation of distillates was carried out using a flow installation at the reaction pressure of 10 atm. and reaction temperature of 350°C, WHSV of raw material was 2.5 h<sup>-1</sup>. Extrudates of catalysts were crashed and sieved to 0.25-0.50 mm fraction. Catalyst load in reactor was 4 grams. Reaction products were analyzed on Hewlett-Packard 5890 GC unit equipped with FID and capillary column DB-1 in accordance with ASTM D-5134-92 method. Identification of peaks was executed by a GS-MSD unit.

## Results And Discussion

Experiments on transformation of distillates with the various thiophene concentrations have shown that during the first 3-5 hours of TOS the conversion of thiophene is close to 100 % (Fig.1). The further carrying out of the process results in a decrease of thiophene conversion, which depends on thiophene concentration in the initial raw material. The increase of thiophene concentration in feedstock from 1.2 wt. % up to 3.5

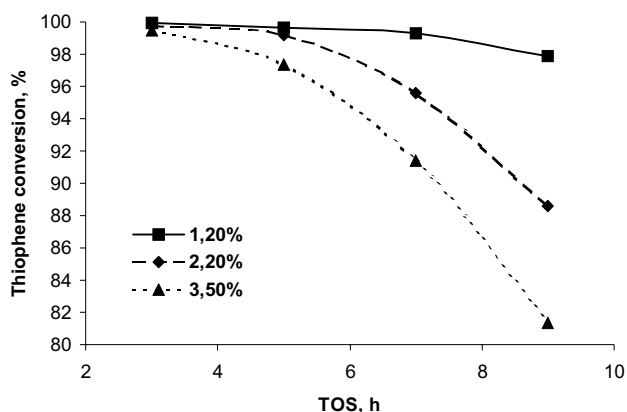


Figure 1. Thiophene conversion at transformation of oil distillates with various thiophene concentrations on catalyst M1.

wt. % results in a decrease of its conversion after 9 hours of TOS from 98 % down to 81 %. The experiment with the distillate containing dibenzothiophene has shown conversion of the latter as low as 0.1 %. Taking into account a decrease of thiophene conversion the total content of residual sulfur in the produced gasoline exceeds allowable level in the most countries [4].

The influence of thiophene concentration in the initial raw material on composition of produced gasoline is shown in Table 1. The difference in composition of the produced gasolines increases depending on TOS of the process. At TOS = 3 hours for distillates varying by thiophene concentration from 0 up to 3.5 wt. %, the contents of n-alkanes in the reaction products are close enough. Further, as the deactivation of the catalyst during the reaction occurs, the concentration of n-alkanes grows proportionally to the thiophene content in a feedstock and after 9 hours of TOS reaches 25 wt. % for the distillate with 3.5 wt. % of thiophene. Changes in concentration of aromatic compounds in the course of the reaction have the opposite trends. Likewise, at TOS = 3 hours, concentrations of aromatic compounds are close enough for all kinds of raw material. Further, concentration of aromatic compounds decreases in time, the rate of lowering being proportional to the thiophene content in a feedstock. It is necessary to note that in all cases the gaseous products of the reaction contain an appreciable amount of hydrogen sulfide. The study of dynamic changes in composition of the produced gasoline has shown that the presence of thiophene in a raw material has an adverse effect on detonation properties of the obtained gasoline (Fig.2). In its composition the amount of high-octane components decreases and that of low-octane components increases with growth of thiophene content in the initial distillate. Figures 1 and 2 show, that the increase of thiophene concentration in a feedstock increases the rate of deactivation of the catalyst which results in decrease of both thiophene conversion and the rate of n-alkanes aromatization.

At present practically all researchers accept that a principal reason of deactivation of a zeolite catalyst in the reactions of hydrocarbons transformation is blocking of active centers by coke deposits. Various authors propose a number of mechanisms of coke formation, the centers of its generation and localization sites of coke on a catalyst surface. Chemical com-

Table 1. The influence of thiophene concentration on composition of producing gasolines.

Thiophene concentration % wt.	Content of n-alkanes % wt., TOS				Content of aromatics % wt., TOS			
	3 h	5 h	7 h	9 h	3 h	5 h	7 h	9 h
0.0	9.73	11.37	14.18	15.11	39.29	35.64	31.25	27.89
1.2	9.32	12.35	16.01	18.93	38.56	33.61	28.48	23.65
2.2	11.81	16.16	18.64	21.47	37.33	29.32	23.59	18.52
3.5	12.23	18.54	21.61	25.01	36.21	26.31	20.65	15.06

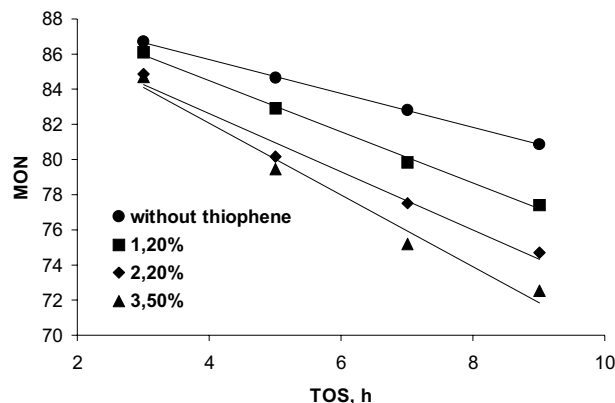


Figure 2. Detonation properties of the produced gasolines at transformation of oil distillates with various thiophene concentrations on catalyst M1.

position and properties of coke depend strongly on reaction conditions, however, in all cases it consists only of carbon and hydrogen. Similar, in our experiments decrease of aromatics yield in the course of the reaction of distillate transformation without thiophene is caused by coke formation. On the other hand, in the case raw material with thiophene the strong increase of the rate deactivation of the catalyst is most likely connected with the additional blocking of active centers by the products of thiophene transformation. Probably, thiophene conversion results either in formation of products deposited on the external surface of zeolite crystals with the subsequent blocking of channels, or in formation of thiophene condensation products in channels of zeolite. In all cases the condensation products contain atoms of sulfur, and a formation of thiophene oligomers in channels of zeolite without elimination of hydrogen sulfide is most probable, as it was shown for HY and silicalite [5].

The mechanism of thiophene transformation on USY zeolite under similar conditions is described elsewhere [6]. Within the frame of this mechanism two main routes relevant for the present study of thiophene transformation on zeolite catalyst are possible, and the initial stage for the both pathways is a formation of carbocation as thiophene adsorbs on Bronsted acid center. The first route should be mainly realized at low molar ratio between thiophene and Bronsted acid center. In this case a concentration of protons is sufficient enough for thiophene transformation to mercaptan through a stage of carbocation formation and further its decomposition to butylene and hydrogen sulfide. In our case this mechanism is most probable for thiophene concentration up to 2.2 wt. % and WHSV – 2.5 h<sup>-1</sup>. At these conditions the most part of thiophene transforms to hydrogen sulfide and butylene that does not result in fast deactivation of the catalyst. At high thiophene concentra-

tion in the raw material, initially formed carbocation because of a lack of protons, has a possibility to react with another thiophene molecule forming condensation products. As a result of this reaction, fast deactivation of the catalyst is observed.

Our results correlate well with the data [6, 7] where the mechanism of thiophene transformation on zeolites HY and H-ZSM-5 has been described. Taking into account our results obtained from FTIR investigations of thiophene adsorption over IC-30-BIMF [8] and data from [5-7], the mechanism of thiophene transformation may be described by the following scheme (Fig.3). The first stage of thiophene transformation is a formation of protonated ring as a result of chemical interaction with the acidic OH groups of zeolite. The next stage is a formation of carbocation, which either decomposes to hydrogen sulfide and butylene, or reacts with another thiophene molecule with formation of hydrogen sulfide, benzothiophene and other products of condensation. Probably, these heavy products block the active centers of zeolite, what results in fast deactivation of the catalyst. This mechanism is valid only for zeolitic component of IC-30-BIMF catalyst because in similar reaction condition thiophene transformation is not observed on alumina, which is a part of the catalyst [8].

For the most complete removal of thiophene and its homologues it is necessary to include a stage of HDS of either initial raw material, or products. As soon as the conditions of HDS and BIMF processes are close enough, the most perspective technique is to use both zeolite catalyst IC-30-BIMF and HDS catalyst in the same reactor.

Figures 4 and 5 show that the use of M2 catalyst for transformation of distillate with 3.5 % wt. of thiophene results in an increase of thiophene conversion on 2-3 % as well as of octane number of the produced gasoline on 2-3 points. Preliminary treating of M2 catalyst by hydrogen sulfide results in increase of both thiophene conversion on 4-6 % and octane number on 4-5 points in comparison with M1 catalyst. This data show, that the most amount of thiophene transforms over zeolite component of M2 catalyst under the scheme described above. Probably, there is no sufficient amount of hydrogen for total removal of sulfur compounds over a HDS component of the M2 catalyst. For the solving of this problem we have co-fed additional hydrogen into a reactor to model a circulation of reaction gases as soon as the yield of hydrogen is 0,5-0,8 wt. % in BIMF process. In this experiment thiophene conversion is close to 100 % and does not change after 9 hours of TOS (Fig.4). Moreover, octane number of the produced gasoline increases on 10-12 points in comparison with M1 catalyst and on 3-4 points in comparison with distillate transformation without thiophene on M1 catalyst (Fig.5). Use of M2 catalyst together with circulation of the reaction gases results also to increase of catalyst stability. Thus, after 9 hours of TOS decrease in the octane number is only 4 points whereas for M1 catalyst this value is 12 points in transformation of distillate with the thiophene content of 3.5 % and 7 points in transformation of initial distillate. In this case the most part of thiophene transforms on the active centers of HDS catalyst by the mechanism shown on Figure 6 [3]. In this case there is no blocking of active centers of zeolite by coke deposits that results in an increase both stability and activity of the catalyst.

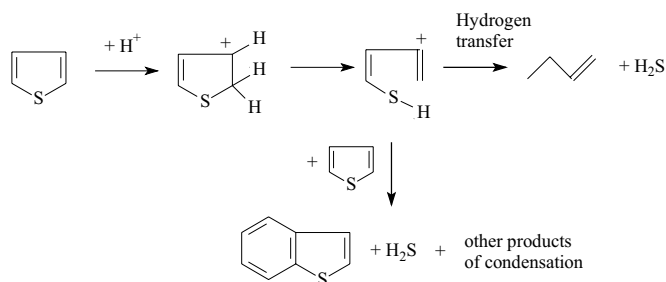


Figure 3. Mechanism of thiophene conversion over zeolite catalyst.

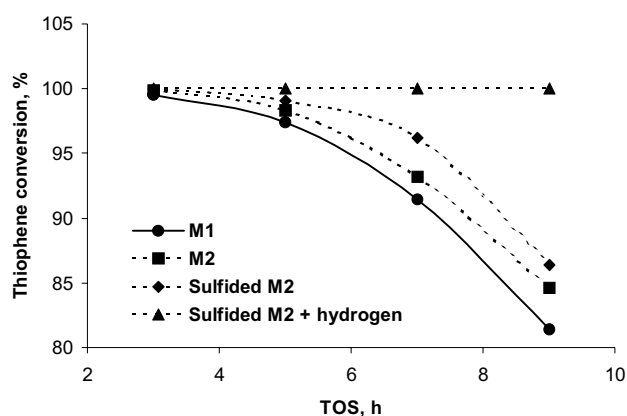


Figure 4. Thiophene conversion at transformation of oil distillate with 3.5 % wt. of thiophene over M1 and M2 catalysts.

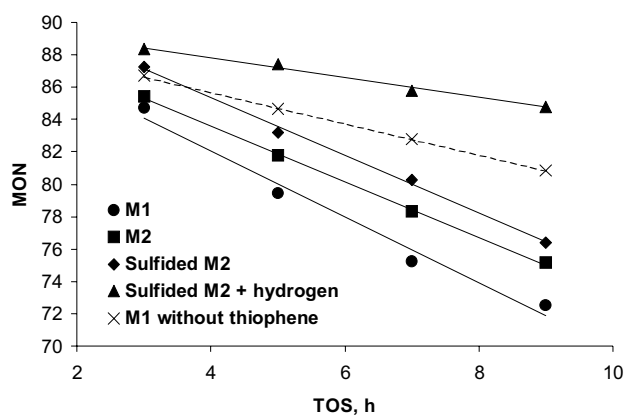


Figure 5. Detonation properties of obtained gasolines at transformation of oil distillate with 3.5 w. % of thiophene over M1 and M2 catalysts.

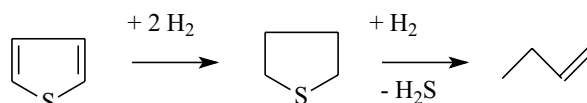
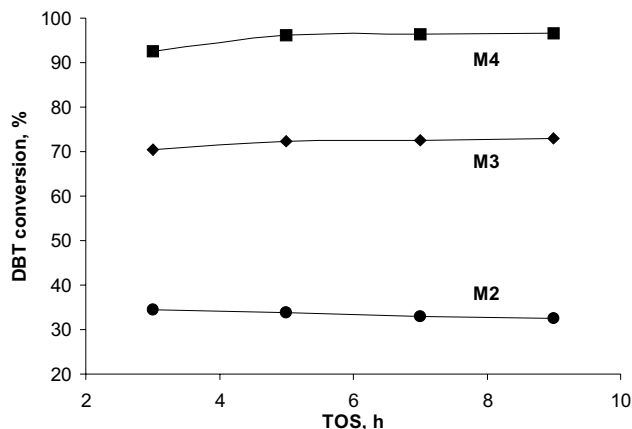


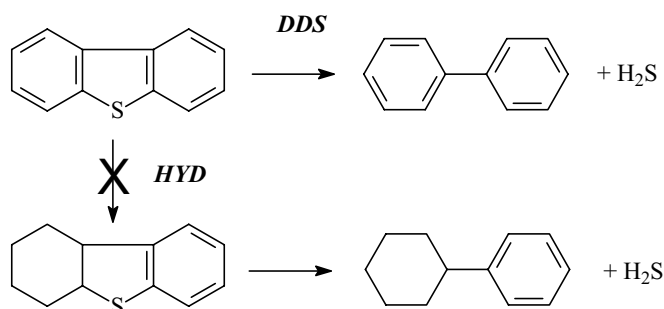
Figure 6. Mechanism of thiophene transformation over HDS catalysts.

However, as shown on Figure 7, conversion of dibenzothiophene on M2 catalyst does not exceed 34 % at transformation of distillate containing thiophene and dibenzothiophene. Thiophene conversion in this experiment is close to 100%. As soon as dibenzothiophene does not react with zeolite catalyst IC-30-BIMF, such low conversion can be explained by two reasons: mild conditions of carrying out the process and/or non-optimal structure of HDS catalyst. So, we have tested Ni-Mo and Co-Mo catalysts with highly dispersed active sites as HDS component (M3 and M4 respectively). Application of M3 and M4 catalysts results in drastically increase of dibenzothiophene conversion. Conversion of dibenzothiophene is 73 % for M3 catalyst (IC-30-BIMF+Ni-Mo/ $\text{Al}_2\text{O}_3$ ) and 97 % for M4 catalyst (IC-30-BIMF+Co-Mo/ $\text{Al}_2\text{O}_3$ ) (Fig. 7). This level of dibenzothiophene conversion allows production of motor fuels with very low sulfur content.

We have found that the major product of dibenzothiophene transformation is biphenyl. A part of other products such as cyclohexylbenzene, tetrahydro- and hexahydrodibenzothiophene does not exceed 2%. This distribution of reaction products indicates that in conditions of the BIMF process dibenzothiophene is transformed through the stage of "direct desulfurization" (DDS) as shown on Figure 8 [10]. Probably, that for dibenzothiophene transformation through the stage of "desulfurization after hydrogenation" (HYD) higher hydrogen pressure is necessary. Formation of cyclohexylbenzene from biphenyl is unlikely because of the presence of sulfur compounds which inhibit reaction of aromatic compounds hydrogenation over HDS component of the catalyst [11].



**Figure 7.** Dibenzothiophene conversion at transformation of oil distillate with 3,5 wt. % of thiophene and 2,5 wt. % of dibenzothiophene.



**Figure 8.** Mechanism of thiophene transformation over HDS catalysts.

## Conclusion

On the results of this work the following conclusions may be draw:

Thiophene can be converted over zeolite catalyst in conditions of the BIMF process. However, increase of thiophene concentration in oil distillates results in fast deactivation of the catalyst and decrease of octane number of the produced gasoline.

Use of a catalyst containing HDS component along with circulation of the reaction gases increases both activity and stability of the catalyst and allows production of motor fuel without sulfur compounds.

Conversion of dibenzothiophene in conditions of the BIMF process is possible when HDS component containing Co-Mo additive with highly dispersed active sites is used.

Under condition of the BIMF process dibenzothiophene is transformed through the stage of "direct desulfurization".

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