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Transformations of thiophene compounds under catalytic cracking conditions

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ABSTRACT

A method for in situ reduction of the sulfur content in catalytic cracking gasoline is reported. A comparison of thermal and catalytic transformations of sulfide and thiophene sulfur is presented. Main transformations of various organosulfur compounds are demonstrated. The effect of [H]-donor activity of hydrocarbons on conversion of thiophene sulfur into hydrogen sulfide is revealed. The impact of acid–base properties of the additives to the cracking catalysts on sulfur content reduction in the liquid products is examined in detail (TPD-NH_3, ^{27}Al NMR, CO_2 adsorption). The choice of optimal qualitative composition of a modifying additive for reducing the sulfur content in catalytic cracking gasoline is substantiated.

1. Introduction

Nowadays, most of petroleum refineries employ catalytic cracking as a main process to provide deep petroleum refining; the fraction of gasoline coming from cracking units constitutes 30–50% of the total gasoline pool at a petroleum refinery [1,2].

Due to increasing environmental requirements to motor fuels, in particular gasoline, the amount of sulfur compounds in fuels should be reduced. The main source of sulfur compounds in commercial gasoline is represented by catalytic cracking gasoline, which accounts for more than 90% of sulfur [1].

The cracking feedstock not subjected to hydrotreatment has a sulfur content of 0.6–4.5 wt.% [3], the amount of sulfur compounds ranging from 10 to 30 wt.%. All organosulfur compounds present in the cracking feedstock can be divided into two main classes: sulfide and thiophene compounds. Sulfide compounds include mercaptans, sulfides, and disulfides – sulfur analogs of alcohols and ethers. Transformations of these compounds under catalytic cracking conditions lead mostly to hydrogen sulfide [4]. The formation of sulfur compounds corresponding to the boiling range of gasoline fraction occurs to a small extent. Thiophenes include all the compounds containing the thiophene ring; they constitute no less than 60–70 wt.% of the feedstock sulfur [4]. Low Lewis basicity and high aromaticity of thiophene compounds underlie their high stability in catalytic cracking [5–7].

Deep hydrotreatment of the feedstock or cracking gasoline is the main process providing a 90% or higher removal of sulfur compounds [8]. Main disadvantage of the cracking gasoline hydrotreatment is a loss in octane number of the resulting product due to hydrogenation of olefins concentrated in the light fractions [9]. To produce gasoline with the sulfur content lower than 10 ppm, more severe hydrotreatment conditions are needed, which decrease the catalyst lifetime and the yield of hydrogenation product [10].

A method based on the development of special compositions of the cracking catalysts for reducing the content of sulfur compounds in the gasoline fraction has been developed in the last decade [11–13]. Such catalysts can decrease the sulfur content in cracking gasoline by 20–30 wt.%. During subsequent hydrotreatment of the produced gasoline, this increase the catalyst lifetime, decreases losses in octane number of gasoline, and improves the yield of hydrogenation product.

In the literature, main emphasis is made on the development and testing of various catalytic systems for decreasing the sulfur content in cracking gasoline. Various compounds were tested as modifying additives to the cracking catalysts: bulk or supported oxides – Lewis acids [13], mixed Mg,Al or Zn,Mg,Al oxides (with a spinel structure) [6,14], modified alumina or titania [7,15], zeolites of different types and their cationic forms [16–18].

The choice of a particular modifying component is not well grounded. Initial ideas substantiating such choice are related

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primarily with a hypothetical interaction of organosulfur compounds having Lewis base properties (unshared electron pair of the sulfur atom) with the active site of an additive, Lewis acid. Such interaction is expected to improve the adsorption strength of a sulfur compound on the active site of the additive; however, the effect of acidity on subsequent transformation was not studied in detail. According to [7], cracking of tetrahydrothiophene requires the presence of paired acid and base sites in the additive.

Subsequently in works [19–24] its proposed that the mechanism of thiophene sulfur removal consists in successive transformation of the thiophene ring via hydrogen transfer into its hydroderivatives, which are then cracked quite readily to hydrogen sulfide [5–7]. Assumption of great importance of hydrogen transfer reactions are confirmed by a large number of publications [5–7,11,14,19–24]. Some alternative mechanisms are also discussed in the literature; they include alkylation of thiophene with olefins [25–27] or self-alkylation to yield polythiophenes [27], and condensation reactions to form polycyclic sulfur compounds [5]. Boiling points of the resulting sulfur-containing products of such reactions exceed the boiling range of gasoline fraction; the formation of sulfur-containing coke is also possible.

Thus, for reduction of sulfur compounds in cracking gasoline is necessary to intensify the selectivity of hydrogen transfer reactions and to increase the concentration of Lewis acid sites of the catalyst. In all these studies little attention is paid to ways of intensification of the hydrogen transfer reactions, as well as their relationship to acid–base properties of catalysts.

The influence of hydrogen transfer reactions on the transformations of organosulfur compounds is closely related with two main factors:

- catalyst activity in these reactions caused by its acid–base properties; and
- [H]-donor ability of a hydrocarbon medium.

Goal of the present work was to study the transformations of thiophene compounds under catalytic cracking conditions and reveal the effect of acid-base properties of catalytic systems and composition of hydrocarbon medium on such transformations.

2. Experimental

2.1. Catalytic systems

In all cases, the industrial equilibrium cracking catalyst (Cat A or e-cat) was used as a reference sample. The catalyst comprised the HREY zeolite as a constant component and a matrix made of amorphous aluminosilicate, aluminum hydroxide and bentonitic clay. The method of catalyst preparation and its properties, as well as the properties of the equilibrium catalyst used in refinery ("Gazprom-ONPZ", Russia, Omsk) are presented in [28].

10 wt.% of a modifying component able to decrease sulfur content was introduced either as a component of the template during catalyst preparation or as an additive to equilibrium catalyst.

The modifying components introduced into the catalyst were represented by ZnZSM-5 or HZSM-5, REY or ZnHREY zeolites, and Mg,Al or Zn,Mg,Al spinels. Hydrotalcites (mixed oxide precursor) were synthesized by the method described in [29]. Table 1 lists the composition of the cracking catalysts under examination.

The additives introduced by mechanical mixing with equilibrium catalyst are conventionally divided into two groups: (1) Lewis acid component (Zn, Zr, Ce, Cr oxides) on an inert support; (2) base component (Ca, Mg oxides) on an inert support. Supports were impregnated with solutions of nitrates, taking 10 wt.% oxide of the indicated metal per a support. Silica, which has no pronounced acid or base properties, was used as a support for additives.

Table 1
Content of components in the samples of cracking catalysts (wt.%).

Catalyst	HREY (wt.%)	Matrix (wt.%)	Special additive
Cat A (e-cat)	18	82	–
Cat B	15	80	5% ZnHREY
Cat C	0	82	18% REY
Cat D	18	78	4% HZSM-5
Cat E	18	78	4% ZnZSM-5
Cat F_x	18	72	10% Mg_xAlO_y[a]
Cat G	18	72	10% $Zn_zMg_xAlO_y$

[a] Oxides with molar ratio Mg:Al = (0.32:1; 0.49:1; 1.90:1; 3.06:1; 3.89:1) were used; for example, by "Cat $F_{0.32}$" refers to sample with Mg:Al = 0.32:1.

The synthesized samples were dried at 100 °C for 12 h with subsequent calcination at 550–750 °C. Before testing, all the samples of model catalysts were treated in 100% water vapor at 760 °C for 5 h.

2.2. Methods for studying the properties of catalytic systems

XRD analysis of the samples was performed on a DRON-3 X-ray diffractometer using $Cu_{K\alpha}$ radiation (λ = 1.5406 Å) with a β-filter. Diffraction patterns were interpreted using the ICDD, PDF-2 (2006) powder diffraction database.

Porous structure of the samples was examined by low-temperature nitrogen adsorption (an ASAP-2020 instrument, Micromeritics), specific surface area (S_{specif}) being determined by the BET method, and total adsorption pore volume (V_{ads}) – from the nitrogen adsorption at $P/P_0 = 0.99$.

The total number of acid sites was found by thermoprogrammed desorption of ammonia (TPD-NH_3) on an AutoChem-2920 high-precision chemisorption analyzer (Micromeritics) using a mixture of 6 vol.% NH_3 in helium. Prior to TPD experiments, samples were heated to 750 °C in a flow of 10 vol.% O_2 in helium, held at this temperature for an hour, and then cooled in flowing helium to 100 °C. Adsorption of ammonia was carried out at the same temperature for 60 min with subsequent blowing off with helium at 100 °C for an hour to remove physisorbed ammonia. TPD of ammonia was conducted in the temperature range of 100–600 °C, heating rate of the measuring cell with a sample was 10 °C/min.

^{27}Al NMR spectra of the solid samples were taken on an Avance-400 (9.4 T) NMR spectrometer (Bruker) with a SB4 multinuclear sensor intended for magic-angle spinning (MAS) experiments at a frequency up to 15,000 Hz with the following parameters of single-pulse experiment: the carrier (Larmor) frequency 104 MHz; pulse width 2.5 μs; pulse-delay time before quantization 6.5 μs; pulse repetition time 0.5 s; total number of pulses 1024; window width 15.6 kHz; and number of points 3000. Spinning rate at a magic angle $54^\circ\ 44'$ was 10^4 Hz. Powdered substances under examination were grinded in an agate mortar and then closely packed without special efforts into spinning rotors (Φ 4 mm) made of zirconia. An 1 M aqueous solution of $AlCl_3 \cdot H_2O$ was used as an external standard.

The concentration ratio of tetrahedrally and octahedrally coordinated aluminum was found from the ratio of integral intensities of characteristics peaks: $\delta_{tetr} \approx 70$ ppm; $\delta_{oct} \approx 7$ ppm [30].

Adsorption of carbon dioxide on the group 2 additives (the base ones) was examined using a Carlo Erba sorptometer at a temperature 273 K and a pressure of CO_2 acid gas ranging from 5 to 80 kPa. In addition, the number of base sites on the surface of synthesized samples was determined by titrating a suspension of solid base in benzene using a 0.10 N solution of bensoic acid in the same solvent [31]. A solution of 1 wt.% phenolphthalein (pK_a = 8.0–9.6) in a mixture of isopropanol and benzene (volume ratio 1:2) was used as an indicator.

2.3. Catalytic testing and analysis of the products

A feedstock were represented by the kerosene–gas oil fraction (boiling range of the fraction 200–350 °C; paraffins ≈40%, naphthenes ≈40%, arenes ≈20%); *n*-undecane, decalin, tetralin, or cumene supplemented with 1.0 wt.% sulfur due to introduction of appropriate sulfur-containing component: dibutyl disulfide (MERCK; >97 wt.%), 2-methyl thiophene (ALDRICH; 98 wt.%) or benzothiophene (MERCK; 99.9 wt.%). The use of kerosene–gas oil fraction is necessary due to its group composition close to the real catalytic cracking feedstock, that allows us to estimate the activity of the studied catalytic systems in the cracking of a real feed.

Catalytic testing was performed at a lab-scale unit with a fixed-bed catalyst (15 g) in the temperature range of 400–550 °C at a catalyst-to-oil mass ratio equal to 2. Thermal (noncatalytic) transformations of model mixtures were carried out in a similar way by loading inert silica ($S_{specif} = 348\ m^2/g$, $V_{pore} = 0.99\ cm^3/g$) instead of catalyst.

The composition of gaseous cracking products was analyzed on a Chromos GH-1000 gas chromatograph equipped with: (a) capillary column (SiO_2, 30 m × 0.32 mm) and flame-ionization detector to determine the composition of hydrocarbon gases (C_1–C_{5+}); (b) packed column (2 m × 3 mm, CaA zeolite) and thermal conductivity detector to measure the content of inorganic components in the gas.

Analysis of liquid products was made on a chromato-mass spectrometer 6890/5973N (Agilent Technologies) with a chromatography column HP-5ms (30 m × 0.25 mm × 0.25 μm). In addition, quantitative composition of the liquid products was determined using a Kristallux 4000M gas chromatograph equipped with a capillary column (ZB-5, 60 m × 0.32 mm × 1.00 μm) and a FPD/FID module including flame photometric detector (FPD) to analyze sulfur compounds and flame ionization detector (FID) to analyze the hydrocarbon moiety. Total sulfur content in the initial feedstock and liquid cracking products was estimated by X-ray fluorescent spectroscopy on an ARL OPTIM'X WD-XRF spectrometer (Thermo Techno).

3. Results and discussion

3.1. Thermal and catalytic transformations of dibutyl disulfide and 2-methyl thiophene in a mixture with n-undecane

As for the observed products, there are four main routes of 2-methyl thiophene transformation during thermal (inert SiO_2) and catalytic (e-cat) cracking of the mixture: (1) formation of hydrogen sulfide, (2) dealkylation to thiophene, (3) isomerization to 3-methyl thiophene, and (4) alkylation and condensation to yield alkylthiophenes, benzothiophenes and dibenzothiophenes.

The rates of thermal transformations by the first three routes are much lower as compared to catalytic transformations (Table 2). In catalytic transformations, the rate of target reaction leading to hydrogen sulfide is nearly three orders of magnitude higher in comparison with that for thermal transformations. During thermal transformations, the aromatic thiophene molecule shows high stability. Even in the presence of *n*-undecane (a hydrogen donor), conversion of 2-methyl thiophene to hydrogen sulfide during thermal tests at 500 °C did not exceed 2% [$k_{500}\ (H_2S) = 1.1 \times 10^{-4}\ s^{-1}$], whereas on equilibrium catalyst at 500 °C it was 48.8% [$k_{500}\ (H_2S) = 3.0 \times 10^{-1}\ s^{-1}$]. A considerable difference in conversions of 2-methyl thiophene to hydrogen sulfide indicates a crucial role of hydrogen transfer from the hydrocarbon donor molecule to thiophene molecule, which proceeds by heterogeneous catalytic route.

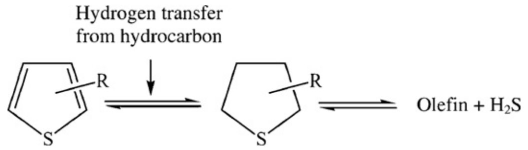

Fig. 1. A scheme of thiophene sulfur transformation under catalytic cracking conditions.

Apparent activation energies for thermal cracking of organosulfur compounds exceed the corresponding values for catalytic transformations (Table 2).

Transformations of alkyl sulfides into hydrogen sulfide are hindered to a much less extent as compared with thiophene compounds. The study of dibutyl disulfide transformation in a mixture with *n*-undecane showed that nearly a 100% conversion of sulfur compounds is observed at a minimum tested temperature of the process (400 °C) in the absence of catalyst. The main route of thermal and catalytic transformations of dibutyl disulfide is the formation of hydrogen sulfide, which yield exceeds 90% as referred to the feedstock sulfur. Thiophene is the second product of the transformation, its thermal stability in comparison with linear sulfides increasing with temperature [4].

3.2. Hydrogen transfer

A possible transformation mechanism of thiophene compounds under catalytic cracking conditions is schematically presented in Fig. 1 [5–7,11,14,19–24].

We adhere to this mechanism and think that hydrogen transfer from the molecule of hydrocarbon donor to thiophene molecule is a key step, since the resulting cyclic sulfides (tetrahydrothiophene and its derivatives) are unstable under catalytic cracking conditions, similar to alkyl sulfides described earlier. The main decomposition product of these compounds is hydrogen sulfide.

3.2.1. Hydrogen donor substances

In hydrogen transfer reactions, various class hydrocarbons can serve as a source of hydrogen. Energy of the C–H bond decreases in a series: C_{arene}–H > $C_{paraffin}$–H > $C_{naphthene}$–H [32]. [H]-donor activity is the integrated feature of hydrocarbons that reflects their activity toward aromatization reactions proceeding under catalytic cracking conditions and the amount of hydrogen released in these reactions. The highest [H]-donor activity is inherent in hydrocarbons with naphthene structures (cyclohexanes, decalins, tetralins); this is caused by their higher activity toward aromatization under catalytic cracking in comparison with *n*-paraffins [32,33] and by a greater amount of stored hydrogen in comparison with arenes (Fig. 2). Within this concept, [H]-donor activity decreases in a series: naphthenes > *n*-paraffins ≫ arenes.

As seen from Table 3, the growth of [H]-donor activity in a series cumene < *n*-undecane < decalin increases both the conversion of aromatic sulfur-containing compound and transition of sulfur into gaseous products, mainly hydrogen sulfide and a small amount of light alkyl mercaptans.

The introduction of additional components in the catalyst also increases the conversion of 2-methyl thiophene and

$$\mathrm{N}\ (390)^{*} \rightarrow \mathrm{Ar} + 6\ [\mathrm{H}]$$

$$\mathrm{P}\ (410) \rightarrow \mathrm{Ar} + 8\ [\mathrm{H}]$$

$$\mathrm{Ar}\ (456) \rightarrow \mathrm{Ar}\ (+\ 0\ [\mathrm{H}])$$

Fig. 2. [H]-donor ability of various class hydrocarbons (N – naphthenes, P – paraffins, Ar – arenes). *The C—H bond energy in a hydrocarbon, kJ/mol, is indicated in brackets.

Table 2
Apparent activation energies and transformation rates of 2-methyl thiophene in a mixture with *n*-undecane into corresponding products.[a]

Testing		H_2S	Th	3-MeTh	*n*-$C_{11}H_{24}$ cracking
Thermal	E_a, (kJ/mol)	203	110	35.9	120
	k_{500} (s^{-1})	1.1×10^{-4}	3.2×10^{-3}	9.1×10^{-3}	5.7×10^{-2}
Catalytic	E_a, (kJ/mol)	101	16.5	25.6	51.5
	$k_{500,}$ (s^{-1})	3.0×10^{-1}	2.9×10^{-2}	1.7×10^{-1}	6.6×10^{-1}

[a] Calculation was made assuming the first order reaction with respect to 2-methyl thiophene and using the equation for isothermal plug-flow reactor $X = 1 - e^{-\mathrm{Kr}}$ k_{500} is the rate constant at 500 °C.

Table 3
Conversion of 2-methyl thiophene and benzothiophene (*X*, %) at a cracking temperature 500 °C.

Catalyst	Hydrocarbon hydrogen donor		
	Cumene [H] = 0/456[a]	*n*-Undecane [H] = 8/410	Decalin [H] = 10/390
	Mixture of 2-methyl thiophene and hydrogen donor		
Cat A (e-cat)	64.8 (1.5)[b]	82.8 (25.6)	99.9 (76.6)
Cat D (HZSM-5)	79.9 (2.1)	90.9 (70.2)	99.9 (96.3)
Cat F ($MgAl_2O_4$)	81.0 (3.3)	94.4 (66.4)	99.9 (88.9)
	Mixture of benzothiophene and hydrogen donor		
Cat A (e-cat)	45.1 (9.3)	63.8 (25.7)	85.7 (70.7)
Cat D (HZSM-5)	56.9 (10.6)	77.3 (61.7)	94.3 (92.2)
Cat F ($MgAl_2O_4$)	59.0 (15.0)	85.1 (69.4)	96.0 (88.1)

[a] The [H]-donor activity: numerator is the amount of stored hydrogen taking into account a reaction yielding cumene, pentylbenzene, naphthalene from cumene, *n*-undecane, and decalin, respectively; denominator is the energy of C—H bond in the initial hydrocarbon, kJ/mol.

[b] The part of sulfur passing into hydrogen sulfide is indicated in brackets.

benzothiophene under the tested conditions as compared to their conversion on equilibrium catalyst. The effect of Mg,Al spinel is more pronounced than that of ZSM-5 zeolite. Distinctions between spinel and zeolite show up also in the apparent activation energies (Fig. 3). This may be related with different types of acidity of the components: HZSM-5 zeolite exhibits a strong Broensted acidity, whereas spinel, having a tetrahedrally coordinated aluminum in its structure, shows a strong Lewis acidity [34,35]. Changes in the type of acidity are known to affect the direction of organosulfur compound transformation. It was demonstrated [5,25–27] that Broensted acidity facilitates the alkylation and polymerization of thiophene compounds. The latter is confirmed by a 1.5–2.5-fold increase in the yield of thiophene alkylation products on a sample with HZSM-5 additive as compared to the spinel-containing catalyst. The values of apparent activation energy for the catalysts with spinel and HZSM-5 zeolite differ nearly by a factor of 2 (76.8 and 134 kJ/mol, respectively), which may reflect a difference in the transformation mechanisms of thiophene compounds into hydrogen sulfide on these catalysts.

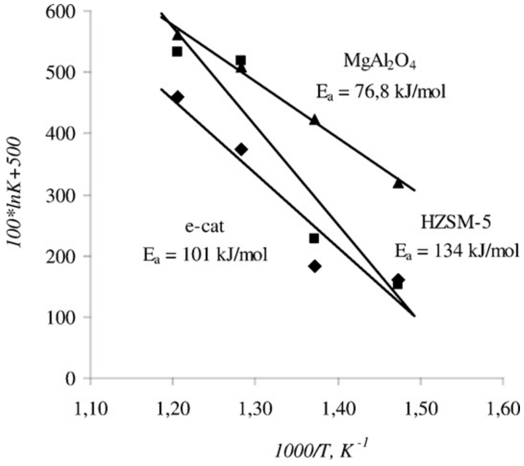

Fig. 3. Temperature dependence of reaction rate constants (in coordinates of the linearized Arrhenius equation) for the H_2S formation proceeding upon cracking of 2-methyl thiophene with *n*-undecane: (1) Cat A (e-cat), (2) Cat D (HZSM-5), (3) Cat F ($MgAl_2O_4$).

During the cracking of 2-methyl thiophene mixtures with tetralin, decalin or *n*-undecane at a minimum tested temperature of the process (400 °C), 2- and 3-methyl tetrahydrothiophenes, which are the intermediates of hydrogen transfer from hydrocarbon molecule to thiophene one, were detected in the liquid products. The presence of such compounds confirms the occurrence of hydrogen transfer reactions with the formation of tetrahydrothiophene intermediate.

Table 4 lists the apparent activation energies and reaction rates for the H_2S formation proceeding upon cracking of 2-methyl thiophene in the mixtures with various hydrogen donor hydrocarbons: tetralin, decalin, *n*-undecane, and cumene. The lowest activation energy is observed in the case of tetralin as an hydrogen donor; with cumene the activation energy is nearly 2 times higher.

3.2.2. Composition of a catalytic system

Another way of controlling the tetrahydrothiophene formation step (Fig. 1) related with hydrogen transfer reactions is to alter the composition of a catalytic system. Additional components are introduced in the cracking catalyst to facilitate hydrogen transfer reactions.

The introduction of Zn, RE cationic forms of Y and ZSM-5 zeolites as well as Mg,Al and Zn,Mg,Al spinels in the catalyst, which are the components catalyzing aromatization reactions [36–39], increases not only the conversion of a thiophene compound, but also the selectivity of target reaction producing hydrogen sulfide.

The contribution of hydrogen transfer reactions during the catalytic cracking can be characterized reliably by isobutane content in a pool of resulting C_4 hydrocarbons [40]. This regularity is caused

Table 4
Apparent activation energies and rates of 2-methyl thiophene transformation into hydrogen sulfide in a mixture with various hydrogen donors.

Hydrogen donor hydrocarbon	k_{500} (s^{-1})	E_a (kJ/mol)
Tetralin	2.1	78.8
Decalin	1.5	91.7
n-Undecane	3.0×10^{-1}	101
Cumene	5.8×10^{-4}	140

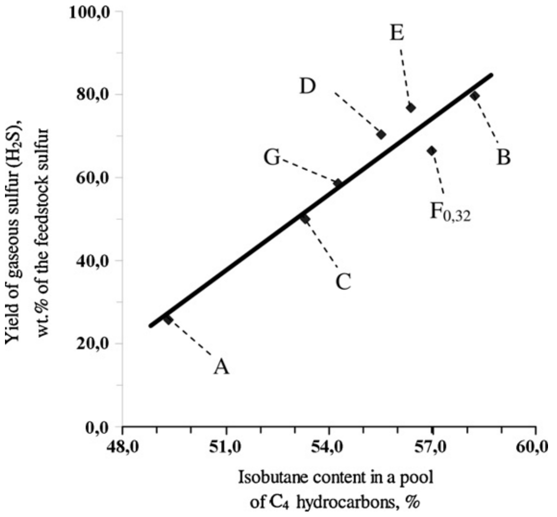

Fig. 4. Effect of isobutane content in a pool of C_4 hydrocarbons on the selectivity of hydrogen sulfide formation upon cracking of 2-methyl thiophene with *n*-undecane on various catalysts at 500 °C.

by predominant formation of isobutane through hydrogen transfer reactions (the interaction of tert-butyl radical with a hydrocarbon donor). Upon cracking of 2-methyl thiophene with n-undecane, an increase in the contribution of hydrogen transfer reactions, which is characterized by isobutane content in the produced C_4 hydrocarbons, raises the selectivity of hydrogen sulfide formation (Fig. 4).

Thus, the most important feature of the cracking catalyst able to reduce sulfur content in gasoline fraction is the ability to catalyze hydrogen transfer reactions, but in the case of zeolite additives (HZSM-5, ZnZSM-5, REY) is an increase of alkyl derivatives formation selectivity.

3.3. Acid–base properties of the catalyst

To study the influence of acid and base active sites of additives on sulfur content in the liquid cracking products, catalytic systems based on MeO/SiO_2 additives were prepared and examined.

According to XRD analysis, all the additives belonging to group 1 are X-ray amorphous. Examination of the porous structure of these samples showed that acidic component (Zn, Zr, Ce, Cr, oxides) introduced in an inert support does not produce considerable changes in main parameters of the porous structure presented in Table 5. This testifies a highly dispersed state of active components on the support surface.

Fig. 5 and Table 6 illustrate the TPD-NH_3 study of the indicated additives. Parameters of acidity are represented by the integral surface area –integral acidity (1), which is related with the number of acid sites, and parameter “$T{\cdot}h$” – the sum of the products of temperature by intensity (2), which characterizes both the total concentration and strength of acid sites:

$$h = \sum [\Delta T_i \cdot h_i]\,, \qquad (1)$$

Table 5
Characteristics of the porous structure of catalytic additives.

Additive	Specific surface area, S_{specif} (m^2/g)	Total pore volume (cm^3/g)	Pore diameter[a] (Å)
SiO_2	348	0.99	114
ZnO/SiO_2	297	0.94	127
ZrO_2/SiO_2	325	0.97	119
CeO_2/SiO_2	322	0.96	119
Cr_2O_3/SiO_2	320	0.98	121

[a] Pore diameter was estimated by the formula $D_{\mathrm{pore}} = 4V_{\mathrm{ads}}/S_{\mathrm{specif}}$.

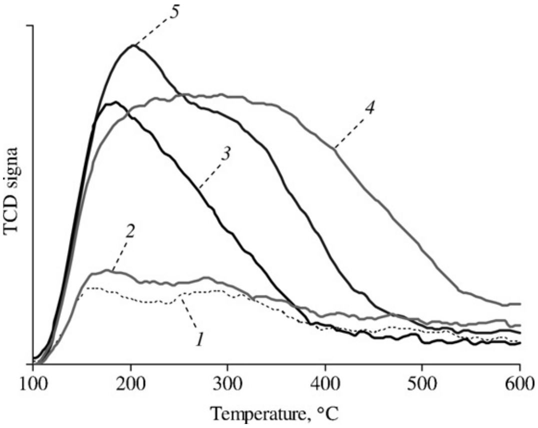

Fig. 5. TPD-NH_3 curves for the additives: *1* – SiO_2, *2* – CeO_2/SiO_2, *3* – ZrO_2/SiO_2, *4* – Cr_2O_3/SiO_2, *5* – ZnO/SiO_2.

$$T \cdot h = \sum [T_i \cdot \Delta T_i \cdot h_i]\,, \qquad (2)$$

where h_i is the intensity reflecting the average number of acid sites with strength *i* over a temperature range ΔT_i; T_i is the average value of characteristic temperature for acid sites with strength *i*. Comparing acidity of the samples, one can see that sample with chromium oxide has the highest values of integral surface area and parameter $T{\cdot}h$; a maximum of the peak is in the high-temperature region, which indicates the presence of a greater number of acid sites that are more strong as compared to other samples. The additives with zinc and zirconium oxides have a more uniform distribution of acid site strength, which is evidenced by peaks in the region of lower temperatures; however, zinc provides a more than 1.5-fold higher acidity.

Estimating the contribution of catalytic additives upon cracking of benzothiophene with *n*-undecane mixture, we found (Fig. 6) that an increase in the surface acidity of an additive decreases sulfur content in the liquid cracking products [$W_{\mathrm{S,l}}, \% = 100{\cdot}S_{\mathrm{l}}{\cdot}\varpi_{\mathrm{l}}/S_{\mathrm{feed}}$, where S_{l} (ppm) – the sulfur content in liquid products, S_{feed} (ppm) – the sulfur content in feedstock, ϖ_{l} – the yield of liquid cracking products]. This confirms that high concentration of Lewis acid sites is necessary to initiate the mechanism of thiophene structures cracking to hydrogen sulfide proposed in [7]. It is well known [41], that the presence of Lewis acid sites facilitates the hydrogen transfer reaction, which in its turn raises the yield of thiophene hydroderivatives. So primary property of special cracking catalyst for reducing sulfur content in gasoline is a high concentration of Lewis acid sites.

To determine the effect of presence of only base sites in the additives the catalytic systems based on oxides of Ca, Mg and Al supported on silica were prepared and examined. The additive Al_2O_3/SiO_2 used as a not containing base sites reference sample.

For the samples with Ca, Mg, Al oxides supported on silica, nonaqueous titration was used to obtain concentrations of the base sites with $H_0 > 8.8$ on the Hammett scale. Adsorption of carbon dioxide at 0 °C and low pressure was also examined for these samples. The calculated Henry constants, which characterize the strength

Table 6
TPD-NH_3 data for the additives.

Sample	Integral parameter $T{\cdot}h$ (100–600 °C), mmol K/g
SiO_2	20.70
ZnO/SiO_2	59.20
ZrO_2/SiO_2	35.65
CeO_2/SiO_2	27.10
Cr_2O_3/SiO_2	82.55

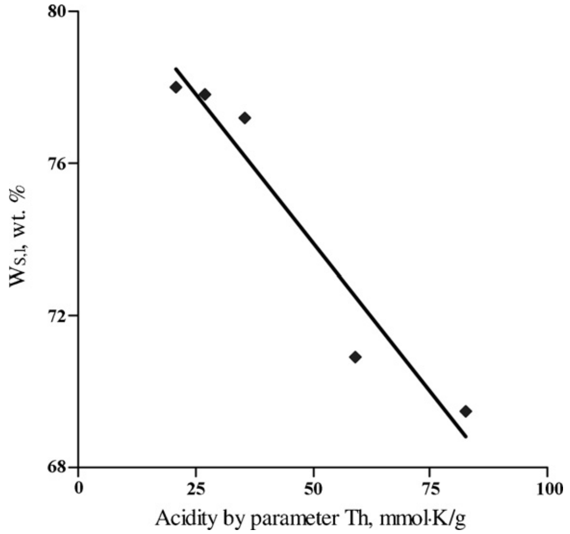

Fig. 6. Effect of acidity of the additive calculated from TPD-NH_3 on a relative sulfur content in the liquid cracking products.

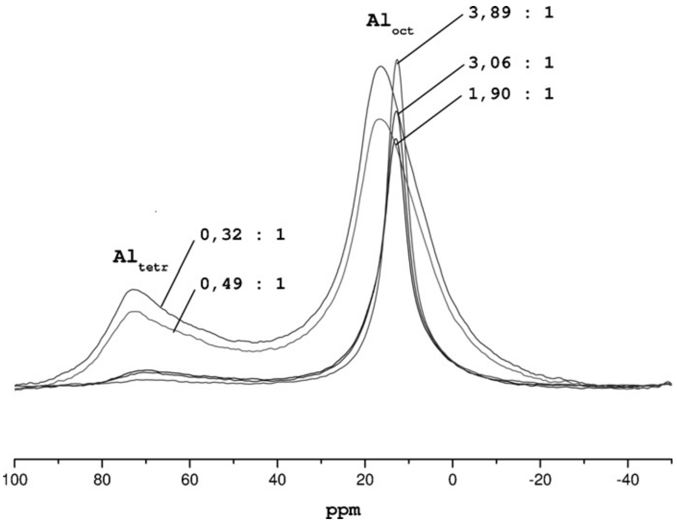

Fig. 8. ^{27}Al NMR spectra of mixed Mg,Al oxides with different Mg:Al molar ratios.

Table 7
Characteristics of catalytic additives basicity.

Additive	Concentration of base sites with $H_0 > 8.8$ (μmol/g)	Henry constant ($\times 10^{-8}$ mol g^{-1} Pa$^{-1)}$)
Al_2O_3/SiO_2	0	1.04
MgO/SiO_2	900	3.52
CaO/SiO_2	1290	13.5

of base sites in the additives, and concentration of base sites are presented in Table 7, adsorption isotherms in the Langmuir coordinates – in Fig. 7.

As follows from Table 7, the deposition of calcium or magnesium oxides on an inert support essentially enhances its base properties: both the concentration and strength of base sites decrease in a series $CaO/SiO_2 > MgO/SiO_2 > Al_2O_3/SiO_2$. Investigation of catalytic properties of the indicated additives upon cracking of *n*-undecane with benzothiophene showed that on catalytic systems with calcium, magnesium and aluminum oxides the liquid products had a residual sulfur content of 81.9, 81.4 and 77.5%, respectively. Thus, if an additive comprise only base sites, this raises sulfur content in the liquid cracking products and does not facilitate sulfur removal.

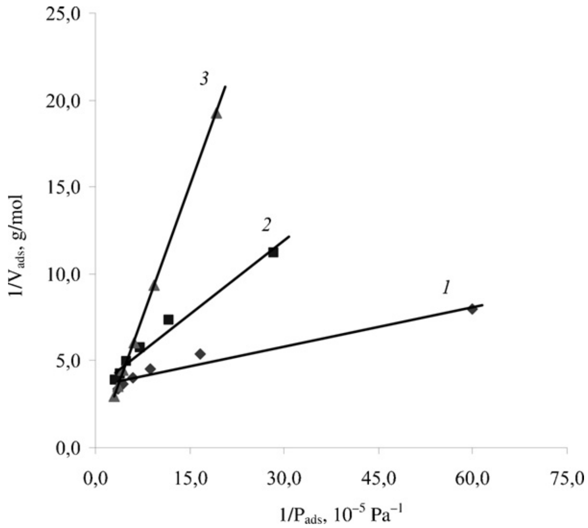

Fig. 7. Adsorption isotherms of carbon dioxide (in Langmuir coordinates) for the additives: *1* – CaO/SiO_2, *2* – MgO/SiO_2, *3* – Al_2O_3/SiO_2.

The catalytic systems based on mixed Mg,Al oxide are more stable and can be used as prototypes for industrial cracking catalyst. Molar ratio Mg:Al in the mixed oxide is known to affect its acid–base properties [42]. Acid properties are caused mainly by the amount and coordination of aluminum cations in the oxide.

As shown by catalytic testing, a decrease in the Mg:Al ratio in the mixed oxide facilitates the reduction of sulfur content in cracking gasoline (Table 8). This can be related with the increasing fraction of tetrahedrally coordinated aluminum cations. Aluminum cation in tetrahedral coordination is a stronger Lewis acid as compared to that in octahedral coordination [35]. This assumption was confirmed by ^{27}Al NMR study of the oxides. Fig. 8 shows ^{27}Al NMR spectra of the mixed Mg,Al oxides. According to Fig. 8 and Table 8, the fraction of tetrahedrally coordinated aluminum cations increases with decreasing the Mg: Al molar ratio in the mixed oxide. The results obtained agree with the phase composition of the samples. For the samples with predominance of magnesium, mixed Mg,Al oxide has the MgO structure, virtually all aluminum cations being octahedrally coordinated. As the content of aluminum rises, this leads to the formation of phases corresponding to spinel structures and γ-form of aluminum oxide. Noteworthy is an increased content of trivalent metal cations in tetrahedral coordinations of the synthesized samples at the Mg:Al ratios equal to 0.32:1 and 0.49:1 in comparison with the normal (non-inverse) bulk magnesium–aluminum spinel [43].

In its turn, a growth of the Al_{tetr} fraction reduces sulfur content in the gasoline fraction. The gasoline yield remaining at a high level.

The deposition of 10 wt.% zinc oxide by impregnation alters the quantitative ratios of aluminum in tetrahedral and octahedral coordination (Fig. 9). Thus, modification of the mixed magnesium–aluminum oxide sample with zinc oxide increases the fraction of tetrahedrally coordinated aluminum and reduces sulfur content in gasoline. Modification of the samples also leads to appearance of magnetically nonequivalent species Al_{oct}. The corresponding absorption is a superposition of at least two signals with different chemical shifts.

Thus, sulfur content in cracking gasoline decreases in direct proportion to the amount of Al_{tetr} in a sulfur reducing component. An increase in acidity of the modifying components facilitates sulfur removal; however, the ability of each modifier to accelerate dehydrogenation and aromatization reactions should be taken into account.

Table 8
Effect of the composition of mixed Mg,Al oxide on the reduction of sulfur content (at 500 °C).

Molar ratio Mg:Al[a]	Fraction of Al_{tetr} cations (%)[b]	Reduction of sulfur content in gasoline (%)[c]	Sulfur in liquid products, $W_{S,l}$ (%)[d]	Phase composition
3.89:1	4	19.3	50	MgO
3.06:1	9	19.5	45	MgO, $MgAl_2O_4$
1.90:1	12	21.3	35	MgO, $MgAl_2O_4$
0.49:1	23	30.1	29	$MgAl_2O_4$, γ-Al_2O_3
0.32:1	25	29.1	25	$MgAl_2O_4$, γ-Al_2O_3

[a] According to chemical analysis.

[b] According to ^{27}Al NMR.

[c] Reduction is calculated relative to e-cat (Cat A): reduction = $(S_{e\text{-}cat} - S_i)/S_{e\text{-}cat} \times 100\%$, where $S_{e\text{-}cat}$ (ppm) – the sulfur content in gasoline produced with using e-cat (Cat A) as a catalyst, S_i – the sulfur content in gasoline produced with using CatF's (with different molar ratio Mg:Al) as a catalyst; mixture kerosene–gas oil fraction with 2-methyl thiophene was used as a feed.

[d] Mixture of *n*-undecane with 2-methyl thiophene was used as a feed.

Mg,Al-mixed oxides contain not only acid sites, but also base sites. According to work [7] this acid–base pair promote reducing of sulfur content in cracking liquid products. However, according to XRD analysis, high-temperature steam treatment of the mixed oxide samples with supported zinc oxide is accompanied by phase transformations leading to compounds with a spinel structure, $(Mg_{1-\lambda}Al_{\lambda})[Mg_{\lambda}Al_{2-\lambda}]O_4$ and $(Zn_{1-\lambda}Al_{\lambda})[Zn_{\lambda}Al_{2-\lambda}]O_4$, and hence by the formation of active sites with Lewis acidity. Acid properties of the indicated samples were characterized in detail by means of ^{27}Al NMR in the corresponding section. Its well known that spinels promote hydrogen transfer reaction.

To validate the effect of hydrogen transfer reactions, we compared properties of the mixed oxide additive with Mg:Al = 0.32:1 and the additive prepared by simultaneous deposition of zinc and magnesium oxides on an inert support $(ZnO + MgO)/SiO_2$, which provides equal concentrations of acid and base sites in the synthesized catalytic systems. Acidity by parameter Th of the $(ZnO + MgO)/SiO_2$ sample is 33.2 mmol K/g; relative sulfur content in the liquid cracking products on such additive attains 80.7 wt.%, exceeding the value (ca. 78 wt.%) calculated from a correlation shown in Fig. 6. A spinel sample obtained from mixed Mg,Al oxide by steam treatment is in agreement with the correlation between surface acidity and relative redistribution of the feedstock sulfur into liquid products: its acidity by parameter Th is 40.1 mmol K/g, and $W_{S,l}$ is equal to 77 wt.%. Analysis of the group composition of liquid products resulting from the cracking of *n*-undecane with benzothiophene on this sample confirms the growing contribution of aromatization reactions: the yield of olefin compounds decreases, whereas the yield of aromatic ones increases.

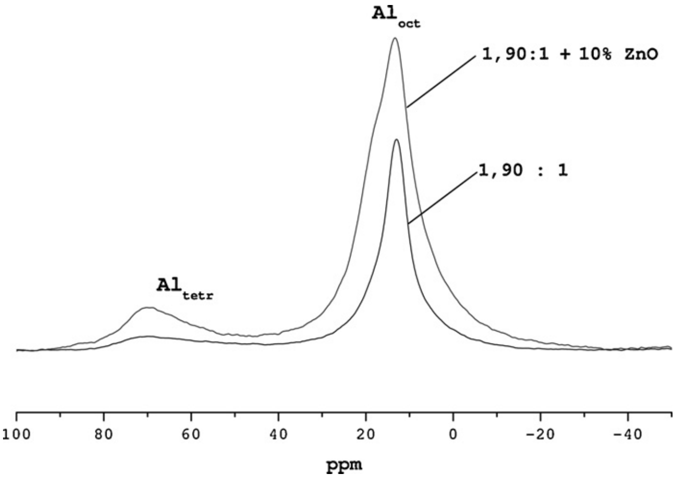

Fig. 9. ^{27}Al NMR spectra of mixed Mg,Al oxide samples: initial and modified with zinc oxide (molar ratio Mg:Al = 1.90:1).

4. Conclusion

Among numerous transformations of alkylthiophenes and benzothiophenes, the hydrogen transfer reactions followed by cracking of thiophene hydroderivatives with the formation of hydrogen sulfide are the most optimal way to reduce sulfur content in cracking gasoline. The contribution of hydrogen transfer reactions can be controlled by two methods: (1) increasing the [H]-donor activity of hydrocarbons present in the cracking feedstock and (2) increasing the catalyst activity in these reactions.

The first method can be used to reduce sulfur content by changing the feedstock composition. It seems reasonable to increase the content of hydrocracking residue or decrease the initial boiling point of the feedstock. This will raise the amount of paraffin and naphthene compounds having a high [H]-donor activity, thus increasing the yield of hydrogen sulfide.

The second method consists in introducing special additives in the cracking catalyst. All of investigated additives promote the hydrogen transfer reactions. These reactions can be promoted by Bronsted (zeolite additives) and Lewis (spinel additives) acid sites. Most promising are the systems containing spinel compounds with a high Lewis acidity. This is confirmed by investigation of the influence of acid–base properties of the additives on sulfur content in the liquid cracking products. The use of HZSM-5 zeolite additive (Bronsted acidity) increases the contribution of thiophene compounds alkylation and secondary cracking of gasoline fraction.

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