

Catalyst Activity in Alkylthiophene Dealkylation

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Abstract—The transformations of 2-alkylthiophenes on various catalysts were studied. In the presence of oxide and sulfide catalysts, 2-methylthiophenes and 2-isopropylthiophenes underwent dealkylation to thiophene. The reaction was complicated by isomerization to 3-alkylthiophene and cracking. The dealkylation of 2-ethylthiophene occurred only in the presence of oxide catalysts. Side-chain dehydrogenation resulting in the formation of 2-vinylthiophene primarily occurred under the action of sulfide and some oxide catalysts. Acid catalysts (amorphous aluminosilicate and zeolites in the form of hydrogen) were the most active and selective in the dealkylation of 2-alkylthiophenes. It is believed that the dealkylation reaction of 2-alkylthiophenes on these catalysts occurs by means of a protolytic mechanism.

INTRODUCTION

Thiophene and its lower homologs can be used as physiologically active substances and starting compounds for the manufacture of dyes, oil additives, polymers, and other valuable chemical products [1]. Thiophene and its lower homologs can be prepared from structurally more complex thiophenes. Analogously to substituted benzenes, alkylthiophenes can be dealkylated in the presence of solid catalysts. Thus, for example, nickel and cobalt supported on aluminum oxide accelerated the demethylation of 2-methylthiophene in the presence of water at $T = 200\text{--}425^\circ\text{C}$; however, the catalysts were rapidly deactivated [2]. 2-Alkylthiophenes ($R = \text{C}_2\text{--C}_5$) were dealkylated to thiophene in 14–35% yield on an alumina–cobalt–molybdenum catalyst in a hydrogen atmosphere at $T = 310^\circ\text{C}$ under pulse conditions; thiophene, 2-ethylthiophene, and 3-ethylthiophene were obtained by the conversion of 2,5-diethylthiophene [3]. 2-Ethylthiophene was converted into thiophene in a yield of no higher than 25% at 30% selectivity in an inert atmosphere under the action of the following: Mg, Al, Ti, and Mo oxides; silicates; an alumina–platinum catalyst; FeCrK; FeCrZn; and tungsten sulfide at $T = 200\text{--}650^\circ\text{C}$ in a pulse unit at $\tau = 0.6$ s. Dehydrogenation and isomerization reactions occurred along with dealkylation [4]. In the presence of Al_2O_3 , amorphous Al, Mg, and Zr silicates, and zeolite HNaY at $T = 500^\circ\text{C}$, 3-methylthiophene was demethylated with simultaneous isomerization to 2-methylthiophene and decomposition. The dependence of catalyst activity and selectivity on catalyst acidity was found for the reaction of 3-methylthiophene. It was found that thiophenes with iso substituents are dealkylated at lower temperatures than thiophenes with normal substituents [5, 6]. On zeolite Y at $410\text{--}490^\circ\text{C}$, methyl-, dimethyl-, trimethyl-, and tetramethylthiophenes were only cracked with the formation of hydrocarbons and hydrogen sulfide [7]. In the

presence of a zeolite catalyst containing 30 wt % rare earth elements with nickel and vanadium impurities, 3-methyl-, 2-ethyl-, 2,5-diethyl-, and 3-hexylthiophenes were converted into thiophene at $T = 500^\circ\text{C}$ and $P = 13$ MPa; however, the selectivity of thiophene formation was no higher than 17% at 2–50% conversion. Isomerization primarily occurred on this catalyst with 65% selectivity. As by-products, 2-ethenylthiophene was formed from 2-ethylthiophene and methyl-, ethyl-, and propylthiophenes and $\text{C}_1\text{--C}_{10}$ hydrocarbons were formed from 3-hexylthiophene [8].

The above data suggest that the dealkylation of alkylthiophenes is not clearly understood. For a long time, the absence of raw materials sources restricted the development of studies in this area. However, more recently [9], it was found that a variety of high-sulfur oils contain thiophenes in considerable amounts (up to 60–100% of the total concentration of sulfur compounds), and efficient methods for separating them were proposed [10]. Moreover, new efficient technologies for the processing of high-sulfur shale from the Volga region have been developed; this provides an opportunity to obtain alkyl-substituted thiophene mixtures in reasonable yields at currently available and newly established refineries [11].

Active and selective dealkylation catalysts should be developed in order to provide a basis for the processing of substituted thiophenes. This is difficult to implement based on the above publications. Various authors performed the reaction under different conditions, and the relevant studies were unsystematic. In a number of cases, the probability of diffusion complications was not taken into account in the determination of catalytic activity. A portion of studies was performed under pulse conditions, and the activity of catalysts was judged only from the yields of thiophene. Because of this, it is difficult to compare the results and to select effective catalytic systems.

Table 1. Activity and selectivity of sulfide catalysts in the reactions of alkylthiophenes at $T = 550^\circ\text{C}$

Sulfide catalyst (S_{sp} , m^2/g)	Dealkylation				2-Ethylthiophene reaction			
	2-methylthiophene		2-isopropylthiophene		dealkylation		dehydrogenation	
	$k \times 10^3$, $\text{ml m}^{-2} \text{s}^{-1}$	S^* , %	$k \times 10^3$, $\text{ml m}^{-2} \text{s}^{-1}$	S^* , %	$k \times 10^3$, $\text{ml m}^{-2} \text{s}^{-1}$	S^* , %	$k \times 10^3$, $\text{ml m}^{-2} \text{s}^{-1}$	S^* , %
TiOS (1.2)	0	0	0	0	0	0	24.7	60
VOS (6)	6.9	50	10.8	24	0.4	0	29.3	67
Cr ₂ S ₃ (13)	2.7	45	2.9	60	0	0	16.5	80
MnS (3.5)	0	0	0	0	0	0	10.7	65
FeOS (3.6)	3.4	4	0	0	0	0	10.9	22
CoS (1.4)	2.1	13	0	0	2.9	3	21.7	30
NiS (0.6)	0	0	0	0	0	0	21.9	80
ZnOS (1.0)	9.1	80	10.7	70	0	0	64.3	75
ZrOS (46)	1.5	76	9.7	87	1.6	39	1.4	37
MoOS (4.5)	3.4	80	4.0	40	0	0	19.0	87
WS ₂ (13)	4.5	35	6.1	44	0	0	17.6	85

* The rest is the selectivity of formation of thiophene cracking products.

In this work, we compared the activity and selectivity of oxide and sulfide catalysts in the dealkylation reactions of structurally different α -substituted thiophenes in the kinetic region using a gradientless method.

EXPERIMENTAL

The sulfides of Mn, Co, and Ni were prepared by precipitation from aqueous metal chloride solutions with hydrogen sulfide, and the sulfide of Cr was obtained by the treatment of CrCl₃ with dry H₂S. WS₂ was prepared by the decomposition of ammonium thion tungstate. The sulfides of Ti, V, Fe, Zn, Zr, and Mo were prepared by the treatment of oxides in a flow of H₂S at $T = 450\text{--}500^\circ\text{C}$ for 2–5 h until constant sulfur concentration in the catalyst was achieved. The resulting sulfides contained an amount of parent oxides (designated as MOS). Table 1 summarizes the specific surface areas of the sulfide catalysts.

Commercial V, Zr, and Zn oxides of reagent and chemically pure grades were used. The oxides of Fe, Mo, and Ti were prepared by the decomposition of iron nitrate, molybdcic acid, and titanium hydroxide, respectively. Stock-produced samples of A-1 γ -Al₂O₃ ($S_{\text{sp}} = 200 \text{ m}^2/\text{g}$) and SiO₂ ($S_{\text{sp}} = 300 \text{ m}^2/\text{g}$) were used. Supported catalysts were prepared by the incipient wetness impregnation of a carrier (γ -Al₂O₃ or SiO₂) with aqueous solutions of ammonium molybdate, vanadyl oxalate, phosphoric acid, hydrofluoric acid, or tungstophosphoric heteropoly acid (HPW).

Commercial CrK/Al₂O₃, CrFe/ZnO, CrK/Fe₂O₃, CaNiP, NaX, and NaY catalysts were used. Decationized zeolites X and Y were prepared by the exchange of sodium ions for ammonium ions followed by thermal treatment. The sodium content of samples was determined by flame photometry. The cationic forms of zeolites with Be, Mg, Ca, and Ba ions were prepared by the replacement of sodium with a corresponding cation from an aqueous nitrate solution followed by thermal treatment. The BET surface of all Y-type zeolites was 500–550 m^2/g , and that of the cation-substituted zeolites was about 300 m^2/g . Before experiments, all of the catalysts were calcined at 500°C for 1 h; oxide and sulfide catalysts were calcined in an oxygen and helium flow, respectively.

Reagent-grade 2-methylthiophene, 2-ethylthiophene, and 2-propylthiophene were used in this study. 2-Isopropylthiophene and 2-*tert*-butylthiophene were synthesized by the alkylation of thiophene with propylene and isobutylene, respectively, in the presence of zeolite CaA at 300°C. The purity of the compounds was monitored by chromatography.

The experiments were performed in a circulation flow setup at a circulating factor of 400 l/h, which sufficed for equalizing reactant concentrations before and after a catalyst bed. Helium from a gas cylinder was supplied to a thermostatted saturator filled with an alkylthiophene and then to a reactor containing a catalyst with a particle size of 0.25–0.5 mm. We found that a further decrease in the catalyst particle size had no

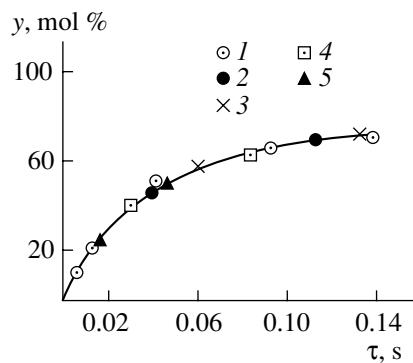


Fig. 1. Effect of contact time on the yield of thiophene in the conversion of 2-methylthiophene on zeolite HNaY at $T = 400^\circ\text{C}$. Initial 2-methylthiophene concentrations (mmol/l): (1) 0.15, (2) 0.11, (3) 0.21, (4) 0.37, and (5) 0.75.

effect on the rate of alkylthiophene conversion; this suggested the occurrence of the reaction in the kinetic region. The entire system, including the reactor, was thermostatted at $T = 160^\circ\text{C}$. The duration of experiment was 1 h. The starting mixture and reaction products were sampled for analysis at regular intervals of 15 min with the use of a six-port valve.

The activity of some sulfide catalysts was experimentally determined in the same setup but without circulation. The analysis was performed on an LKhM-8MD chromatograph with a thermal-conductivity detector (a column $(2\text{ m} \times 3\text{ mm})$ packed with Porapak Q and Porapak R (1 : 1)).

The contact time (τ , s) is equal to the ratio of catalyst volume (cm^3) to gas flow rate (cm^3/s) at room temperature and atmospheric pressure. The contact time was changed by varying the catalyst amount and the gas flow rate. Based on the results of analysis, the alkylthiophene conversion (x , %), yields of products (y , mol %), selectivity ($S = y/x$, %) at $x = 50\text{--}60\%$, rate of reaction (w , mol h^{-1} (g Cat^{-1})), and first-order reaction rate constant (k , $\text{ml m}^{-2} \text{s}^{-1}$) were calculated.

RESULTS AND DISCUSSION

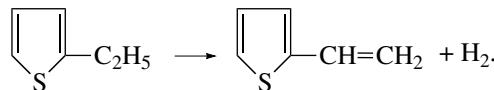
The dealkylation of 2-alkylthiophenes at $T = 250\text{--}600^\circ\text{C}$ occurred only in the presence of catalysts. The reaction was performed on catalysts analogous to those used in the high-temperature processes of hydrocarbon conversion, for example, dehydrogenation, cracking, and dealkylation. Because oxide sulfidization is probable to occur under the action of a reaction medium, experiments with sulfide samples were also performed.

Sulfide catalysts. Table 1 summarizes the results of a study on the conversion of 2-methylthiophene, 2-ethylthiophene, and 2-isopropylthiophene at $T = 550^\circ\text{C}$.

In the presence of the majority of sulfide catalysts (except for Ti, Mn, and Ni sulfides), 2-methylthiophene was converted into thiophene with a simultaneous release of hydrogen sulfide, hydrogen, methane, and

small amounts of $\text{C}_2\text{--C}_4$ hydrocarbons and coke formation.¹ The sulfides of Ti, Mn, Ni, Co, and Fe were inactive in the conversion of 2-isopropylthiophene. Dealkylation resulting in the formation of thiophene, propylene, and by-products (hydrogen, hydrogen sulfide, and $\text{C}_2\text{--C}_4$ hydrocarbons) occurred on the other catalysts. Alkyl-group migration to another position (isomerization) occurred in no case. The selectivity of thiophene formation on some sulfide catalysts was as high as 80–87%. The rates of dealkylation of 2-methylthiophene and 2-isopropylthiophene were of the same order of magnitude.

The dealkylation of 2-ethylthiophene occurred at a low rate only in the presence of Co, Zr, and V sulfides. The selectivity of thiophene formation on zirconium sulfide was 39%, and it was no higher than 0–3% on the other sulfides. On all of the test metal sulfides, 2-ethylthiophene decomposed with the release of hydrogen sulfide, gaseous hydrocarbons, hydrogen, and coke without detectable isomerization. The dehydrogenation reaction primarily occurred with the formation of 2-vinylthiophene:



Oxide catalysts. The conversion of 2-methylthiophene, 2-ethylthiophene, and 2-isopropylthiophene on various oxide catalysts was studied at $T = 450\text{--}500^\circ\text{C}$. In preliminary experiments, it was found that the conversion of alkylthiophenes on various oxide catalysts and the yield of thiophene are independent of the concentration of a parent compound (for example, see Fig. 1). Therefore, the activity of catalysts was characterized by a first-order reaction rate constant.

2-Ethylthiophene, which bears a normal substituent, was converted into dealkylation, isomerization, and dehydrogenation products (Table 2). Dealkylation occurred on all of the test catalysts. Molybdenum trioxide was the most active in the removal of the ethyl group from the thiophene ring; however, the selectivity of thiophene formation was only 24%. Amorphous and crystalline aluminosilicates were less active but more selective: in the presence of these catalysts, the selectivity of thiophene formation was 44–70%. The other oxide catalysts were ineffective in the dealkylation of 2-ethylthiophene. Only Al_2O_3 , $\text{MoO}_3/\text{Al}_2\text{O}_3$, and zeolites accelerated the reaction of 2-ethylthiophene isomerization to 3-ethylthiophene (the selectivity was 8–51%). In the presence of molybdenum trioxide, the dehydrogenation of 2-ethylthiophene to 2-vinylthiophene occurred with low selectivity. The $\text{CrK}/\text{Al}_2\text{O}_3$, CrFe/ZnO , $\text{CrK}/\text{Fe}_2\text{O}_3$, and CaNiP supported binary oxide catalysts, which are commonly used in hydrocar-

¹ Henceforth, the cracking of alkylthiophenes is characterized by the yield of H_2S .

Table 2. Conversion of 2-ethylthiophene in the presence of oxide and zeolite catalysts at $T = 500^\circ\text{C}$

Catalyst	Dealkylation		Isomerization		Dehydrogenation	
	$k \times 10^3, \text{ml m}^{-2} \text{s}^{-1}$	$S, \%$	$k \times 10^3, \text{ml m}^{-2} \text{s}^{-1}$	$S, \%$	$k \times 10^3, \text{ml m}^{-2} \text{s}^{-1}$	$S, \%$
$\gamma\text{-Al}_2\text{O}_3$	0.6	14	2.6	51	0	0
TiO_2	6.0	15	0	0	0	0
MoO_3	22.0	24	0	0	12	13
$\text{MoO}_3/\text{Al}_2\text{O}_3$	6.0	14	3.5	8	7.4	17
$\text{Cr-K/Al}_2\text{O}_3$	0.9	12	0	0	6.6	89
Cr-Fe/ZnO	3.0	4	0	0	46	70
$\text{Cr-K/Fe}_2\text{O}_3$	2.0	2	0	0	68	62
CaNiP	0.1	1	0	0	6.0	50
AlSi^*	2.0	70	0	0	0	0
HNaX	11.0	60	—	—	0	0
CaY	6.9	53	2.1	16	0	0
HNaY	8.4	44	6.9	36	0	0

Note: The reactions were accompanied by the cracking of thiophenes.

* Amorphous aluminosilicate.

Table 3. Activity and selectivity of oxide catalysts and zeolite HNaY in the conversion of 2-methylthiophene and 2-isopropylthiophene at $T = 500^\circ\text{C}$

Catalyst	2-Methylthiophene				2-Isopropylthiophene			
	dealkylation		isomerization		dealkylation		isomerization	
	$k \times 10^3, \text{ml m}^{-2} \text{s}^{-1}$	$S^*, \%$	$k \times 10^3, \text{ml m}^{-2} \text{s}^{-1}$	$S^*, \%$	$k \times 10^3, \text{ml m}^{-2} \text{s}^{-1}$	$S^*, \%$	$k \times 10^3, \text{ml m}^{-2} \text{s}^{-1}$	$S^*, \%$
$\gamma\text{-Al}_2\text{O}_3$	0.1	30	0.06	16	1.6	50	0.2	6
$\gamma\text{-Al}_2\text{O}_3\text{ HF}$	0.7	57	0.4	30	—	—	—	—
$\text{V}_2\text{O}_5/\text{SiO}_2$	3.4	74	0	0	1.1	45	0	0
$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$	4.6	70	0	0	1.8	52	0	0
AlSi^{**}	0.1	46	0.08	30	3.6	89	0.7	11
HNaY	8.1	48	3.8	23	30.4	97	0.1	3
$\text{H}_3\text{PO}_4/\text{SiO}_2$	0.2	12	2.1	75	—	—	—	—
HPW/SiO_2	0.5	18	4.5	80	—	—	—	—

* The rest is the selectivity of formation of thiophene cracking products.

** Amorphous aluminosilicate.

Table 4. Activity and selectivity of zeolites in the conversion of 2-methylthiophene at $T = 450^\circ\text{C}$

Catalyst*	Dealkylation		Isomerization		Cracking	
	$w \times 10^4$, mol h^{-1} (g Cat) $^{-1}$	S , %	$w \times 10^4$, mol h^{-1} (g Cat) $^{-1}$	S , %	$w \times 10^4$, mol h^{-1} (g Cat) $^{-1}$	S , %
BeNaY (0.6)	13.0	33	19	48	4.1	11
MgNaY (0.7)	17.0	62	2.9	11	4.8	17
CaNaY (0.7)	14.0	57	4.0	17	4.0	16
BaNaY (0.6)	1.4	58	0.4	17	0.4	16
NaY	0.2	50	0.1	25	0.1	25
HNaY (0.4)	5.0	56	1.8	20	2.0	22
HNaY (0.6)	11.0	30	16.0	42	8.2	23
HNaY (0.75)	19.0	37	19.0	37	12.0	24
HNaX (0.6)	10.0	42	8.0	33	5.0	21

* The figures in parentheses indicate the degree of deactionization of zeolite NaY or the degree of Na substitution for a divalent cation.

bon dehydrogenation, were more effective in the dehydrogenation reaction: the selectivity of 2-vinylthiophene formation was 50–89%. Amorphous aluminosilicate and zeolites were inactive in the dehydrogenation of 2-ethylthiophene.

The activity and selectivity of oxide catalysts in the conversion of 2-methylthiophene and 2-isopropylthiophene depended on catalyst composition (Table 3). The products of 2-methylthiophene conversion were thiophene, 3-methylthiophene, H_2S , $\text{C}_1\text{--C}_4$ hydrocarbons, coke, and hydrogen. 2-Isopropylthiophene was converted into thiophene, propylene, small amounts of $\text{C}_2\text{--C}_4$ hydrocarbons, and traces of 3-isopropylthiophene. Aluminum oxide exhibited low activity, and it was nonselective in dealkylation and isomerization reactions. However, it exhibited clearly pronounced cracking activity. The introduction of hydrofluoric acid into $\gamma\text{-Al}_2\text{O}_3$ decreased its cracking activity and increased dealkylating and isomerizing activities. In the conversion of 2-methylthiophene, V_2O_5 supported on aluminum oxide or silica gel exhibited sufficiently high activity and was selective in thiophene formation. However, this was less typical of the conversion of

2-isopropylthiophene, and the performance characteristics of processes were lower. In the presence of amorphous aluminosilicate and deactionized zeolite Y, 2-methylthiophene was converted into dealkylation, isomerization, and cracking products. In the case of 2-isopropylthiophene, the predominant reaction was dealkylation: the selectivity of thiophene formation was 97%.

Zeolite catalysts. The conversion of 2-methylthiophene was also performed in the presence of cationic forms of zeolites (Table 4). Partial replacement of sodium by Be, Mg, or Ca in zeolite NaY resulted in a catalyst that exhibited high activity in dealkylation and increased selectivity toward thiophene formation. The formation of surface proton sites is also inevitable upon replacement of sodium by a divalent cation in zeolite NaY. Alkylthiophene conversion can occur under the action of both proton and aprotic cation sites. The participation of cations in dealkylation is evidenced by the fact that the rate of methyl group elimination from 2-methylthiophene increased with the degree of calcium substitution for sodium in zeolite Y (Fig. 2). The acceptor ability of Be^{2+} , Mg^{2+} , and Ca^{2+} cations, which is characterized by ionization potentials, is higher than that of Ba^{2+} [12]; zeolites BeNaY, MgNaY, and CaNaY are superior to BaNaY in dealkylation activity.

The zeolites in hydrogen form were active in the dealkylation of alkylthiophenes (Table 4). The zeolite in sodium form (NaY) exhibited low activity in the conversion of 2-methylthiophene. Decationization of the zeolite increased its activity toward dealkylation reactions, as well as towards isomerization and decomposition. The higher the degree of deactionization, the greater this effect. This was likely because the proton acidity of the zeolite increases with the degree of deactionization [6]. Zeolite HNaY deactionized by 80% was

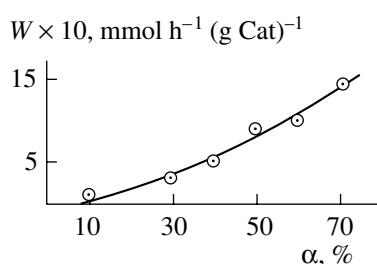


Fig. 2. Dependence of the rate of dealkylation of 2-methylthiophene on the degree of substitution of calcium ions for sodium ions (α) in zeolite NaY.

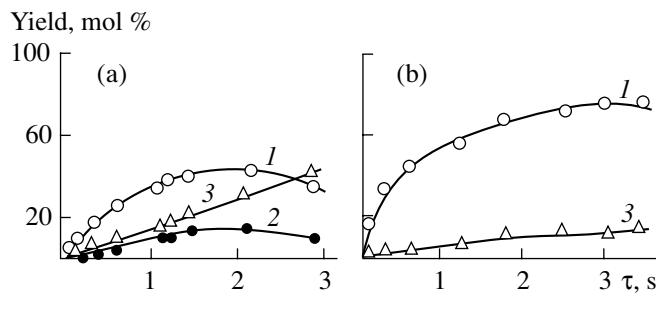


Fig. 3. Effects of contact time on the yields of products of (a) 2-methylthiophene conversion on zeolite HNaX at $T = 400^{\circ}\text{C}$ and (b) 2-isopropylthiophene conversion on amorphous aluminosilicate at $T = 450^{\circ}\text{C}$: (1) thiophene, (2) 3-methylthiophene, and (3) hydrogen sulfide.

more active than the initial sodium form NaY by two orders of magnitude. These results indicate that proton sites play an important role in the conversion of 2-methylthiophene. This was also supported by our experiments in which phosphoric and tungstophosphoric acids supported on SiO_2 were used as catalysts (Table 3). The dealkylation reaction is reversible; the reverse reaction is thiophene alkylation with olefins. Both of the reactions are accelerated by analogous acid catalysts [13].

As mentioned above, catalysts with no strong proton sites but with strong aprotic sites, for example, aluminum and vanadium oxides, are active in the dealkylation reaction (Table 3). Moreover, it was found that oxide catalysts such as AlCrK and FeCrK (in which the occurrence of proton sites can hardly be assumed because of high alkali metal contents) exhibited activity in dealkylation (Table 2). The dealkylation of 2-methylthiophene on AlSiK at $T = 500^{\circ}\text{C}$ occurred at approximately the same rate as on an acidic aluminosilicate (w was equal to 214 and $280 \times 10^{-9} \text{ mol h}^{-1} \text{ m}^{-2}$, respectively). Some metal sulfides accelerated alkylthiophene dealkylation; in this case, the rates of reactions, for example, of 2-methylthiophene and 2-isopropylthiophene on the same sulfide catalyst were similar (Table 1). These results suggest that the reaction does not occur by a heterolytic mechanism. However, additional study is required for determining the mechanism of dealkylation with the participation of aprotic sites.

The above results suggest that the reactions of 2-alkylthiophene dealkylation occur under the action of catalysts of different nature. In the presence of a number of transition metal sulfides, 2-methylthiophene and 2-isopropylthiophene underwent dealkylation. However, these catalysts are unsuitable for the removal of normal radicals, in particular, ethyl from 2-ethylthiophene, because side-chain dehydrogenation primarily occurs in the presence of metal sulfides. The dealkylation of 2-alkylthiophenes with structurally different substituents in the presence of Al_2O_3 and transition-

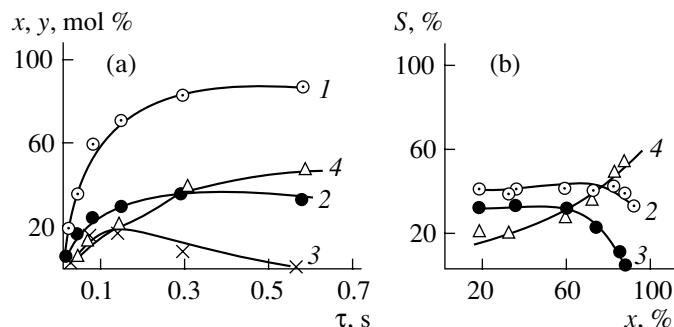
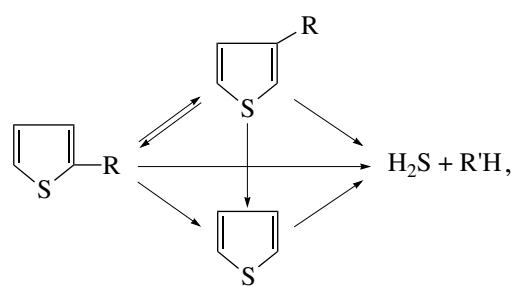


Fig. 4. Conversion of 2-ethylthiophene on an HNaY catalyst at $T = 450^{\circ}\text{C}$: (a) dependence of (1) 2-ethylthiophene conversion (x) and the yields (y) of (2) thiophene, (3) 3-ethylthiophene, and (4) hydrogen sulfide on contact time; (b) dependence of the selectivity of (2) thiophene, (3) 3-ethylthiophene, and (4) hydrogen sulfide formation on 2-ethylthiophene conversion.

metal oxides is an insufficiently selective process. Catalysts containing proton acid sites, in particular, amorphous aluminosilicates and decationized zeolites, are effective in dealkylation.

In the conversion of 2-methylthiophene and 2-ethylthiophene in the presence of decationized zeolites HNaY, the yield of decomposition products increased with contact time. In this case, the yields of thiophene and 3-alkylthiophenes increased to a particular limit and then changed only slightly (for example, see Figs. 3, 4). 2-Isopropylthiophene underwent dealkylation to thiophene and cracking, whereas isomerization almost did not occur. For example, the selectivities of thiophene and 3-alkylthiophene formation remained unchanged as the conversion of 2-ethylthiophene increased to 60–80% (Fig. 4); these selectivities decreased at a higher conversion. The selectivity of cracking product formation continuously increased with alkylthiophene conversion. The shape of kinetic curves allowed us to conclude that the conversion of alkylthiophenes occurs in accordance with a parallel and consecutive reaction scheme. At a low conversion, the parent alkylthiophene reacts via independent paths: (1) the elimination of an alkyl group from the thiophene ring, (2) the migration of the alkyl to another position (isomerization), and (3) the elimination of sulfur. As the conversion increases, the resulting thiophenes also undergo elimination:



where $R = \text{Me}$, Et , or $i\text{-Pr}$; $R'\text{H}$ is methane, ethylene, or propylene for thiophenes with $R = \text{Me}$, Et , and $i\text{-Pr}$, respectively.

This reaction scheme does not reflect the formation of by-products: hydrogen, $C_2\text{--}C_4$ hydrocarbons, etc.

By varying the conditions of dealkylation on HNaY , we found that the maximum yield of unsubstituted

Alkylthiophenes		
$w, \text{ mmol h}^{-1} (\text{g Cat})^{-1}$	0.7	0.8
$S, \%$	40	47

Thus, thiophenes with *tert*-butyl and isopropyl radicals underwent dealkylation at a higher rate and selectivity than those with normal radicals. The stability of alkyl cations increased in the same order [14]. An analogous effect of the nature of radicals on the reactivity of alkylthiophenes in dealkylation and isomerization reactions was observed on other aluminosilicate catalysts [6]. Based on these data, the dependence of the activity of catalysts on proton acidity, and the fact that the thiophene ring is readily protonated [15], we assume

thiophene was 30–75% at 42–97% selectivity depending on the structure of the parent alkylthiophene (Table 5).

In the presence of zeolite HNaY , the rate of dealkylation and the selectivity of thiophene formation depended on alkyl-chain length and branching. Thus, the following results were obtained on zeolite HNaY with a degree of decationization of 80% at $T = 250^\circ\text{C}$:

1.0	2.0	11.7
48	83	94

that the dealkylation reaction on decationized zeolites occurs with the participation of surface protons by a carbonium-ion mechanism. The rate of 2-alkylthiophene isomerization also depends on the Brønsted acidity (Table 4). Therefore, it is believed that, in the presence of catalysts with proton acid sites, the reactions of dealkylation and alkyl-group migration occur by a protolytic mechanism, for example, in accordance with the following reaction scheme:

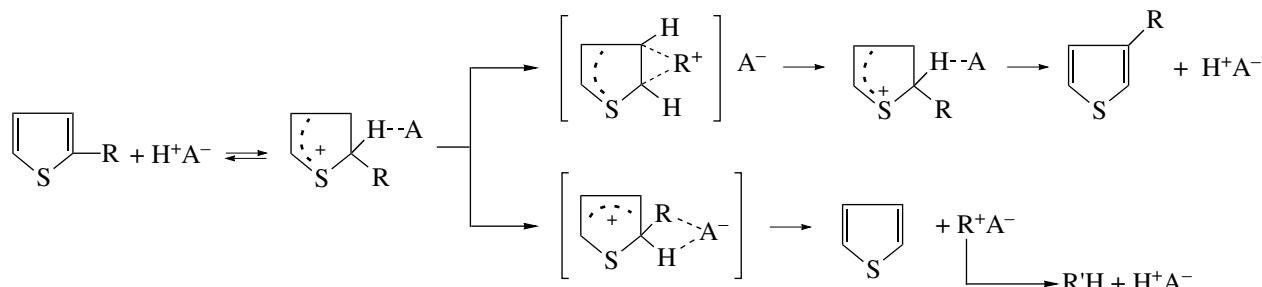


Table 5. Dealkylation of 2-substituted thiophenes in the presence of zeolite $\text{HNaY}(0.8)$

R	$T, ^\circ\text{C}$	τ, s	Thiophene yield, mol %	Selectivity for thiophene formation, %
Methyl	400	0.29	35	58
"	500	0.14	35	64
Ethyl	400	0.86	34	41
"	450	0.29	37	44
"	500	0.14	35	42
<i>n</i> -Propyl	350	0.11	30	42
<i>iso</i> -Propyl	300	0.11	56	94
"	400	0.14	72	90
"	450	0.09	75	91
"	500	0.04	73	97
<i>tert</i> -Butyl	250	0.86	70	94

It is well known [14] that an analogous mechanism is typical of dealkylation in isomerization reactions of compounds from the benzene series. This is related to similarity in the chemical properties of thiophenes and alkylbenzenes, which exhibit an aromatic character. However, thiophenes differ from alkylbenzenes in that aromatic conjugation in the former gets broken for various reasons with conversion into diene compounds. These diene compounds are readily decomposed at the C–S bond resulting in the elimination of hydrogen sulfide and hydrocarbons.

REFERENCES

1. Belen'kii, L.I., Zakharov, E.P., Kalik, M.A., Litvinov, V.P., Stoyanovich, F.M., Taits, S.Z., and Fabrichnyi, B.P., *Novye napravleniya khimii tiofena* (New Areas in Thiophene Chemistry), Gol'dfarb, Ya.L., Ed., Moscow: Nauka, 1976.
2. Balandin, A.A., Sovalova, L.I., and Slovokhotova, T.A., *Dokl. Akad. Nauk SSSR*, 1958, vol. 120, no. 4, p. 775.

3. Kuzyev, A.R., *Kataliticheskii sintez organicheskikh soedinenii sery* (Catalytic Synthesis of Organosulfur Compounds), Novosibirsk: Inst. Kataliza, 1979.
4. Mashkina, A.V. and Chernov, V.I., *Neftekhimiya*, 1969, vol. 9, no. 3, p. 445.
5. Chernov, V.I. and Mashkina, A.V., *Kinet. Katal.*, 1969, vol. 10, no. 2, p. 307.
6. Chernov, V.I. and Mashkina, A.V., *Kinet. Katal.*, 1971, vol. 12, no. 4, p. 985.
7. Shan, H.H., Li, C.Y., Yang, C.H., Zhao, H., Zhao, B.Y., and Zhang, J.F., *Catal. Today*, 2002, vol. 77, nos. 1–2, p. 117.
8. Leflaive, P., Lemberton, J.L., Perot, G., Mirgain, C., Carriat, J.Y., and Colin, J.M., *Appl. Catal. A*, 2002, vol. 227, nos. 1–2, p. 201.
9. Siraeva, I.N., Ulendeeva, A.D., Parfenova, M.A., Nikitina, T.S., and Lyapina, N.K., *Neftepererab. Neftekhim.*, 2002, no. 9, p. 33.
10. Kuz'menko, I.S., *Cand. Sci. (Chem.) Dissertation*, Tomsk: Inst. of Petroleum Chemistry, 2000.
11. Blokhin, A.I., Zaretskii, M.I., Stel'makh, G.P., and Eivazov, G.S., *Novye tekhnologii pererabotki vysokosernistykh slantsev* (New Technologies for Processing High-Sulfur Shale), Moscow: Svetlyi Stan, 2001, p. 179.
12. *Spravochnik khimika* (Chemist's Handbook), Leningrad: Goskhimizdat, 1962, vol. 1, p. 325.
13. Shuikin, N.I. and Lebedev, B.L., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, no. 5, p. 1154.
14. Skarchenko, V.K., *Alyumosilikatnye katalizatory* (Silica-Alumina Catalysts), Kiev: Akad. Nauk USSR, 1963.
15. Belen'kii, L.I., *Poluchenie i svoistva organicheskikh soedinenii sery* (Synthesis and Properties of Organosulfur Compounds), Moscow: Khimiya, 1998, p. 344.