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Activity of Catalysts in Thiophene Synthesis from Furan and Hydrogen Sulfide

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Abstract—Thiophene synthesis from furan and H_2S over acid catalysts is reported. Proton donor catalysts are low-active, nonselective, and prone to deactivation. Alumina-supported catalysts having Lewis acid sites, such as alumina-supported catalysts, are more efficient. With these catalysts, the thiophene formation rate per Lewis acid site increases with increasing site strength. It is assumed that the reaction proceeds via the formation of a surface intermediate consisting of an acid site bonded to an α carbon atom of the furan ring and an H_2S molecule nondissociatively adsorbed on a basic site. At atmospheric pressure, $T = 250$–450°C, initial furan concentrations of 1–20 vol %, and H_2S/furan = 0.4–20 (mol/mol), the thiophene formation reaction is first-order with respect to both reactants and its rate constant increases with increasing temperature. The thiophene formation rate depends on the H_2S/furan molar ratio. Under optimal conditions, the thiophene yield is 95–98 mol % and the thiophene formation rate is high.

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Thiophene and its derivatives are important organosulfur compounds. They are usable as physiologically active substances; dyes; oil additives; and starting chemicals in the synthesis of polyorganosiloxanes, polymers, stabilizers, vulcanization accelerators, etc. Unsubstituted thiophene can be synthesized from various compounds via noncatalytic reactions, but catalytic methods are more promising. These include the reactions of hydrogen sulfide with acetylene, butadiene, butene, and butane. However, these reactions take place under conditions such that thiophene formation is accompanied by the deep cracking of organic compounds, which causes early catalyst deactivation [1]. Thiophene can be synthesized from furan, which is obtained from furfurol. The latter is produced in quantity from pentosan-containing wastes from agriculture, forestry, and woodworking. Under the action of a catalyst, furan reacts with hydrogen sulfide to yield thiophene [2, 3]. This reaction was carried out at atmospheric pressure, $T = 300$–600°C, and a contact time of 40–70 s in the presence of activated carbon, a copper–carbon catalyst, or alumina (unmodified or modified with chromium, copper, or thorium oxide). The best results were obtained at $T = 400$°C with unpromoted alumina. In the presence of this catalyst, the thiophene yield was 31–37 mol %. This reaction yielded large amounts of by-products. The reaction carried out over alkali-metal forms of zeolites (NaX, LiNaX, NaY, LiNaY) in a pulsed reactor at $T = 420$°C and a contact time of 0.4 s yielded thiophene in 70–75 mol % yield. The catalysts underwent deactivation during the reaction, but they could be regenerated [4–6]. In the presence of the sulfide catalyst (5% Co, 16% Mo)/Al_2O_3 at $T = 200$–350°C, $P = 2.8$ MPa, H_2S/furan = 12 : 1 (mol/mol), and a furan + H_2S feed rate of 0.2–2.1 g h^{-1} (g Cat)$^{-1}$, the thiophene yield ranged between 35 and 78% and the thiophene selectivity was 40–78% [7]. In the presence of alumina modified with 2.5% potassium phosphotungstate at $T = 300$–400°C, $P = 0.9$–1.6 MPa, a furan GHSV of 16–54 h^{-1}, and H_2S/furan = (3–6) : 1 (mol/mol), the thiophene yield was 72–93 mol % and the thiophene selectivity was 85–93% [8]. However, furan cyclization in the H_2S medium has not been studied systematically. The data available on this reaction are insufficient to establish a correlation between the activity and the properties of catalysts, and it is, therefore, difficult to design an efficient process for thiophene synthesis from furan and hydrogen sulfide.

Here, we report the interaction between furan and hydrogen sulfide over acid–base catalysts of different compositions.

EXPERIMENTAL

All chemicals were reagent- or pure-grade. Hydrogen sulfide (99.5%) was obtained by reacting H_2 with S over an AlNiMo catalyst. The following commercial catalysts and supports were used: γ-Al_2O_3 (S_{sp} = 200, 250, and 300 m^2/g), SiO_2 (S_{sp} = 310 m^2/g), zeolite NaX, and the decationized zeolites HZSM-5 (Si/Al = 100, S_{sp} = 500 m^2/g) and HNaY (S_{sp} = 800 m^2/g).

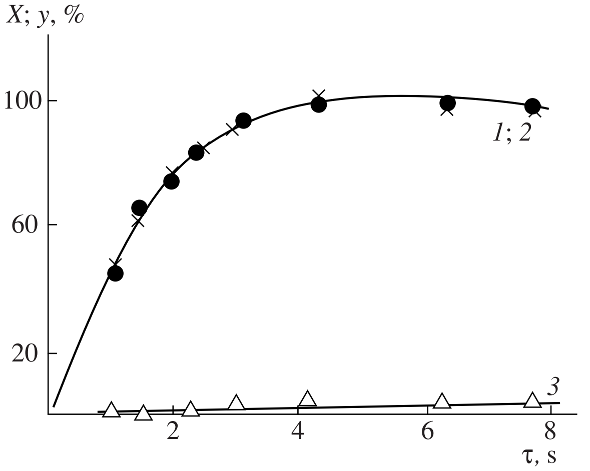


Fig. 1. Effects of the contact time on the (*1*) furan conversion, (*2*) thiophene yield, and (*3*) gaseous by-product yield (W/Al_2O_3 catalyst, $T = 400°C$, $C_0 = 1.3–1.5$ vol %, $M = 6.5–7.1$).

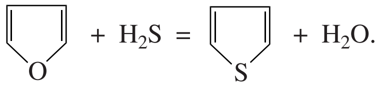
Supports were calcined at $T = 500°C$ for 5 h. Supported catalysts were prepared by incipient-wetness impregnation of a support with an aqueous solution of an acid (phosphoric, sulfuric, hydrofluoric, or silicotungstic (HSiW)), ammonium tungstate, ammonium molybdate, chromium nitrate, or sodium hydroxide. Impregnated supports were dried in air at 110°C for 5 h and were then calcined in flowing air for 5 h: zeolites NaX and NaY and silica gel–supported phosphoric acid were calcined at 400°C; the other catalysts, at 500°C. The catalyst $HSiW/SiO_2$ was calcined at 300°C in flowing helium. The following catalysts were examined (metal or acid wt % in parentheses): WO_3/Al_2O_3 (7), B_2O_3/Al_2O_3 (1.3), Cr_2O_3/Al_2O_3 (0.5), MoO_3/Al_2O_3 (10), Cr_2O_3/SiO_2 (1.5), Na/Al_2O_3 (0.01, 0.03, 0.14, 0.6), H_2SO_4/Al_2O_3 (2.2), H_3PO_4/SiO_2 (30), HF/Al_2O_3 (3), and $HSiW/SiO_2$ (25). The acid–base properties of these catalysts were studied earlier by IR spectroscopy using pyridine, CO, and $CDCl_3$ adsorption techniques [1, 9]. The strength of sites (in kJ/mol) was estimated as follows: protonic sites, as the pyridine affinity of the proton (PA^a); basic sites, as $CDCl_3$ deuterium affinity (PA^b); Lewis acid sites (L-sites), as the heat of CO adsorption (Q_{CO}).

Experiments were carried out at atmospheric pressure in a flow reactor connected to a chromatograph. Helium from a cylinder was fed into a furan-filled bubbler cooled to 0°C. Furan-saturated helium and an H_2S + He mixture or pure H_2S from another cylinder were fed into a gas blender. The resulting gas mixture was fed into the reactor filled with a catalyst and crushed glass and heated in a fast furnace. For higher reactant concentrations in the reactor, the furan-filled bubbler was cooled to 0 or –20°C and undiluted H_2S was passed through it. In the experiments requiring a low furan concentration, the gas leaving the bubbler was diluted with helium. Half an hour after the admission of the reactants into the reactor, the initial mixture and the reaction products were sampled for chromatographic analysis (LKhM-8MD chromatograph, thermal-conductivity detector, 2 m × 3 mm column packed with Porapak Q + R (1 : 1)). Chromatograms were recorded in a temperature-programmed mode at $T = 50–180°C$. In each run, we used a fresh catalyst sample with a particle size of $d = 0.25–0.5$ mm. The reaction was kinetically controlled, as was indicated by the fact that the reaction rate was the same at $d < 0.25$ mm. The time on stream was usually 1 h; in some cases, it was extended to 3 h.

The contact time (τ, s) was taken to be equal to the ratio of the catalyst bed volume (cm^3) to the gas flow rate (cm^3/s) at atmospheric pressure and room temperature. From chromatographic data, we derived the furan or hydrogen sulfide conversion (X, %), the product yields (y, mol %), the thiophene selectivity ($S = y/X$, %), the average furan conversion rate per gram of the catalyst (w, mmol h^{-1} (g Cat)$^{-1}$), the same rate per protonic site (w_{H^+}, μmol/h), the same rate per L-site (w_L, μmol/h), and the first-order rate constant (k, s^{-1}). The measurement error was ±5 rel %.

RESULTS AND DISCUSSION

Calculations demonstrate the thermodynamic possibility of furan recyclization into thiophene:



The equilibrium furan-to-thiophene conversion is 100% at $T < 700$ K and 99.7–96.5% at $T = 700–1000$ K. We found experimentally that thiophene does not form from furan and H_2S at 400°C without a catalyst. In the presence of a catalyst, this reaction yields no by-products under certain conditions. At high temperatures and high furan conversions, the evolution of carbon monoxide and ethylene takes place. It is likely that other products also result from the reaction and are adsorbed by the catalyst surface.

At a constant temperature, initial furan concentration (C_0), and H_2S/furan ratio (M), extending the contact time raises the furan conversion and the yields of thiophene and gaseous by-products for all catalysts (see, e.g., Fig. 1).

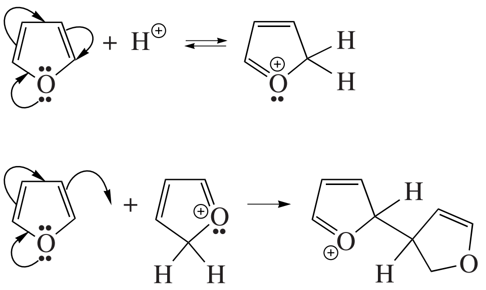
The synthesis of thiophene over various catalysts was carried out at $T = 400°C$, $C_0 = 1.3–2.2$ vol %, an H_2S excess of $M = 6.3–7.2$, and various τ values. In catalyst comparison, the measure of catalytic activity was the reaction rate over the first hour.

Table 1. Activity and selectivity of proton donor catalysts in thiophene synthesis from furan and H_2S at $T = 400°C$, $C_0 = 1.4–1.6$ vol %, and $M = 6.4–7.1$

Catalyst (S_{sp}, m^2/g)	PA^a, (C_{H^+})*	τ, s	X, %	y, mol %	S, %	Thiophene formation rate	
						w, mmol h^{-1} (g Cat)$^{-1}$	w_{H^+}, μmol/h
SiO_2 (300)	1390 (2.8)	9.7	15	0	0	0	0
H_3PO_4/SiO_2 (40)	1300 (1.2)	9.6	0	0	0	0	0
$HSiW/SiO_2$ (305)	<1180 (1.0)	7.0	40	34	85	0.26	0.8
HZSM-5	1180 (0.4)	6.1	100	27	27	0.22	1.2
HNaY	1200 (0.2)	1.8	85	11	13	0.30	1.9

* PA^a is the strength of the protonic sites, kJ/mol; C_{H^+} is the concentration of these sites, μmol/m^2.

Table 1 lists experimental data for the catalysts dominated by protonic sites. The activity of these catalysts is low, so the reaction had to be conducted at a long contact time (τ = 6–10 s). On the silicon dioxide surface, which contains a large number of very weak acid sites, the furan conversion is as low as 15% even at τ = 10 s and no thiophene is formed. The introduction of phosphoric acid into SiO_2 somewhat increases the acidity of the surface, but the resulting catalyst is absolutely inactive in furan conversion into thiophene. The modification of SiO_2 with silicotungstic heteropoly acid generates strong protonic sites on the surface. The resulting catalyst accelerates the conversion of furan into thiophene with a thiophene selectivity of 85%. However, the rate of this reaction is very low (both per gram of the catalyst and per protonic site). It is possible that the activity of this catalyst depends on the presence of not only protonic sites, but also sites resulting from the decomposition of the heteropoly acid in the hydrogen sulfide medium (tungsten cations) [10]. For the hydrogen forms of zeolites HZSM-5 and HNaY, which contain very strong protonic sites, the selectivity of thiophene formation from furan and H_2S and the rates w and w_{H^+} are low. It is possible that the activity of these zeolites is again due to the small number of strong L-sites present on the surface ($C_L = 0.1$ μmol/m^2, $Q_{CO} = 41–55$ kJ/mol) rather than to the protonic sites. Coke was detected on the surface of the zeolite catalysts after the run. As the time on stream was extended from 45 to 90 min, the rate of furan conversion on zeolite HNaY decreased by a factor of 1.5 and the thiophene selectivity increased by a factor of 1.7. This suggests that zeolite deactivation is mainly due to furan decomposition. Furan is known to undergo decomposition and polymerization under the action of solutions of inorganic acids [11]. It is likely that the protonation of the α carbon atom of a furan molecule yields an acid and this acid then attacks another furan molecule to cause polymerization:



and so on.

A similar effect is likely exerted by the protonic sites of the zeolites. Thiophene, unlike its homologues, is stable in the presence of catalysts with strong protonic sites, such as HNaY, at least up to 450°C [12].

The catalysts dominated by L-sites turned out to be more active in thiophene formation (Table 2). In the presence of zeolite NaX without a binder, which has weak Lewis acid sites and moderately strong basic sites with PA^b = 800–900 kJ/mol, the furan conversion is 80% and the thiophene selectivity is 86% at $T = 400°C$, τ = 7.4 s, $C_0 = 2.2$ vol %, and $M = 4.7$. In the presence of NaX with a binder, the thiophene selectivity is higher ($S = 95\%$), apparently because of the presence of the aluminum-containing component. With the Cr_2O_3/SiO_2, which has weak L-sites (chromium ions), furan recyclization into thiophene proceeds slowly and nonselectively. At $T = 400°C$, $C_0 = 1.5$ vol %, $M = 6.3$, and τ = 5.4 s, the thiophene yield is 27 mol %, $S = 64\%$, and the reaction is complicated by the formation of large amounts of by-products.

High activity and high selectivity in thiophene synthesis are shown by alumina-supported catalysts containing strong L-sites (mainly Al^{3+} cations). They are much more active than the catalysts containing both

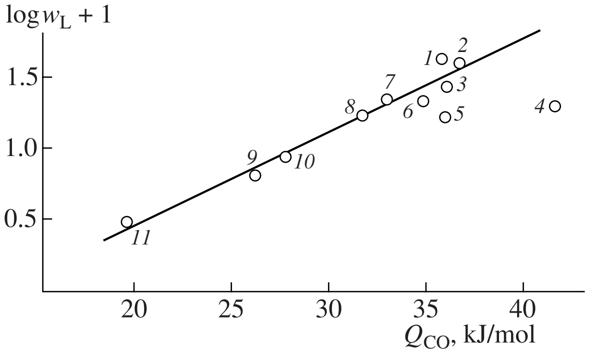


Fig. 2. Logarithm of the thiophene formation rate per L-site (w_L) as a function of the L-site strength (T = 400°C, $C_0 \sim$ 1.5 vol %, $M \sim 7$). The catalyst numbering is the same as in Table 2.

protonic sites and weak Lewis acid sites. The catalysts B_2O_3/Al_2O_3 and WO_3/Al_2O_3 contain L-sites of nearly the same strength as the catalysts MoO_3/Al_2O_3 and H_2SO_4/Al_2O_3, but the former are more active in thiophene formation. The catalyst HF/Al_2O_3 has very strong L-sites, but its activity is comparatively low. This decrease in catalytic activity may be due in part to the fact that strong protonic sites complicating the process are present on the surface of these catalysts (C_L = 0.1–0.3 μmol/m^2). However, it is more likely that the acid components, which reduce the strength and concentration of basic sites [9], make difficult hydrogen sulfide activation. The introduction of sodium hydroxide into alumina raises the basicity of the catalyst [1, 9] and decreases its activity by reducing the strength of its L-sites. The higher the sodium hydroxide content of the catalyst, the stronger this effect. The sample containing 0.6 wt % Na is almost inactive.

These data suggest that the activity of a catalyst in the thiophene formation reaction is determined by the strength of its acid–base pair and that the main factor is the Lewis acidity of the surface. The reaction rate per L-site increases with an increasing strength of the L-sites (Table 2, Fig. 2).

Quantitatively, the correlation between the reaction rate and the L-site strength is unsatisfactory because it ignores the fact that L-sites of different strengths are involved in thiophene synthesis and that protonic and basic sites also make some contribution to the reaction. Furthermore, surface sulfuring (which is inevitable under our experimental conditions) is known to reduce the L-site concentration and to block basic sites [13]. Nevertheless, this correlation points to the significance of Lewis acid sites in furan recyclization into thiophene. Thus, thiophene synthesis from furan and hydrogen sulfide requires catalysts having strong L-sites conjugated with moderately strong basic sites, in particular, alumina-supported catalysts.

The mechanism of thiophene formation from furan and H_2S is almost unknown. It was assumed that the catalyst surface causes furan ring opening at the C–O

Table 2. Activity and selectivity of catalysts dominated by Lewis acid sites* in thiophene synthesis from furan and H_2S (T = 400°C, C_0 = 1.3–1.5 vol %, M = 6.3–7.2)

Entry	Catalyst (S_{sp}, m^2/g)	Q_{CO} (C_L)**	Thiophene formation rate	
			w, mmol h^{-1} (g Cat)$^{-1}$	w_L, μmol/h
1	WO_3/Al_2O_3 (280)	36 (1.6)	1.7	3.8
2	B_2O_3/Al_2O_3 (290)	36 (1.6)	1.8	3.9
3	Cr_2O_3/Al_2O_3 (200)	36 (2.4)	1.1	2.3
4	HF/Al_2O_3 (195)	42 (2.0)	0.7	1.8
5	MoO_3/Al_2O_3 (260)	36 (0.7)	0.3	1.6
6	H_2SO_4/Al_2O_3 (230)	35 (2.0)	1.0	2.2
7	0.01 Na/Al_2O_3 (200)	33 (3.3)	1.3	2.0
8	0.03 Na/Al_2O_3 (200)	32 (3.0)	0.9	1.5
9	0.14 Na/Al_2O_3 (190)	26 (3.8)	0.5	0.7
10	Cr_2O_3/SiO_2 (370)	28 (1.0)	0.3	0.8
11	NaX	20 (3.0)	0.6	0.3

*The alumina-based catalysts modified with W, Cr, HF, Mo, and H_2SO_4 contain strong protonic sites with PA^a < 1300 kJ/mol (0.1–0.15 μmol/m^2) along with L-sites.

**Q_{CO} is the strength of the L-sites, kJ/mol; C_L is the concentration of these sites, μmol/m^2. These data refer to the sites dominating the surface.

bond [3], and this hypothesis was later confirmed by adsorption studies. Furthermore, it was thought that furan decomposition is preceded by the formation of a bond between the catalyst and the furan oxygen atom [6, 11, 14]. This was assumed to be followed by the addition of a hydrogen sulfide molecule to the resulting dangling bond with the formation of a mercaptooxy compound molecule, which was thought to undergo dehydration under the action of the catalyst to form a thiophene ring.

Apparently, the ring oxygen atom is not involved in furan activation in the presence of solid catalysts whose surface is not rich in strong protonic sites. Because of aromatic conjugation, the α carbon atoms of furan have a higher electron density, which facilitates their interaction with electrophilic agents, such as coordinatively unsaturated surface cations. Hydrogen sulfide can be adsorbed both nondissociatively and dissociatively on the catalyst surface. Protonic sites are incapable of activating H_2S. The L-sites of catalysts (e.g., Al_2O_3 and NaX) can chemisorb H_2S dissociatively, but only at low surface coverages. At H_2S coverages above 0.4 mmol/(g Cat), the IR spectrum indicates the presence of only H_2S species nondissociatively bound to basic sites [1, 12, 13]. In our experiments, the amount of hydrogen sulfide per gram of catalyst was 2–3 orders of magnitude larger. Furthermore, in furan recyclization over catalysts having L-sites, the thiophene yield increases greatly as the H_2S/furan molar ratio is raised. For example, for the W/Al_2O_3 catalyst at $T = 400°C$, $C_0 = 8.5$ vol %, and $\tau = 2$ s, the thiophene yield is 42% for $M = 3$ and 86% for $M = 11$. These data suggest that nondissociatively adsorbed hydrogen sulfide is involved in furan recyclization into thiophene.

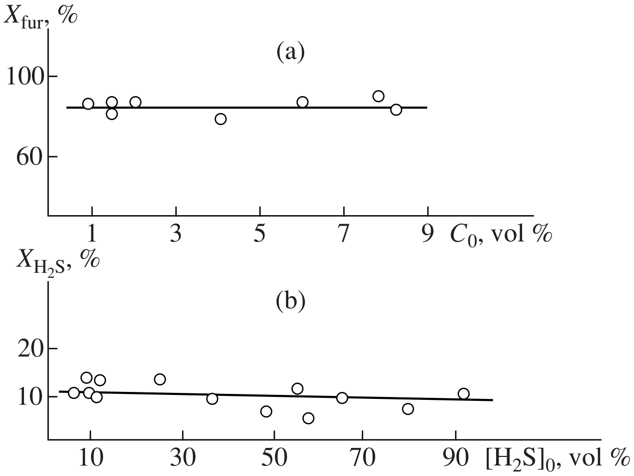


Fig. 3. Conversion of (a) furan and (b) hydrogen sulfide as a function of their initial concentration (B/Al_2O_3 catalyst, $T = 400°C$, $\tau = 1.7–2.0$ s).

The dependence of the activity of the catalysts on their surface acidity and the data available on furan and H_2S chemisorption suggest the following mechanism for the catalysts containing L-sites: The contact between a furan molecule and the catalyst results in a coordination bond between an acid site of the surface and one α carbon atom of the ring (because of the planar orientation of the furan molecule on the catalyst [11, 15, 16], it is not impossible that the other α carbon atom forms a similar bond). The activated furan molecule adds an H_2S molecule nondissociatively adsorbed

Table 3. Effects of the contact time and furan concentration on the furan conversion in the H_2S medium at $T = 400°C$

τ, s	C_0, vol %	M	X, %	y, mol %	S, %	k_{fur}, s^{-1}
0.4	1.5	6.8	26	26	99	0.8
0.8	1.6	6.1	43	42	98	0.7
1.1	1.3	7.1	59	58	98	0.8
1.7	1.6	6.9	73	70	97	0.8
2.0	1.4	7.0	86	83	97	1.0
2.4	1.5	7.0	88	85	96	0.9
3.0	1.6	6.7	93	92	98	0.9
1.9	1.0	8.0	85	82	96	1.0
2.0	1.6	6.9	83	79	95	0.9
2.0	4.1	6.8	78	77	99	0.8
2.0	7.8	7.3	90	88	98	1.1
2.0	8.3	11.0	88	85	97	1.1
1.1	4.3	18	87	84	97	1.9

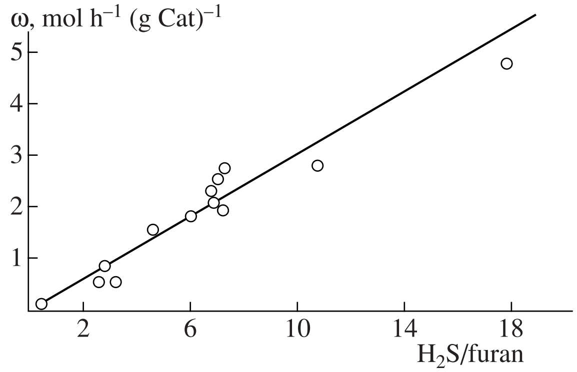
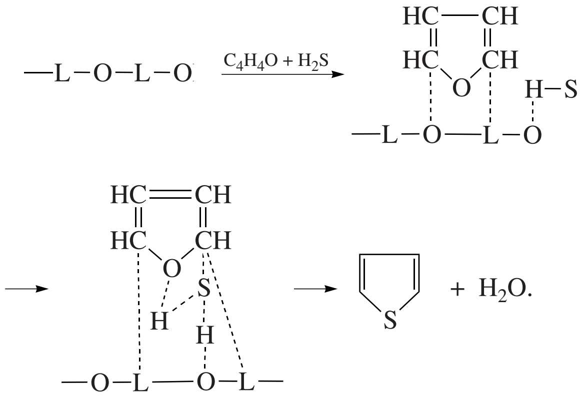


Fig. 4. Thiophene formation rate as a function of the H_2S/furan molar ratio (B/Al_2O_3 catalyst, $T = 400°C$, C_0 = 2 vol %).

on a basic site. The dehydration of the resulting surface intermediate yields thiophene:



It is also likely that this surface intermediate undergoes partial decomposition to release carbon monoxide and, possibly, an unsaturated thioaldehyde. The latter is the source of coke deposits on the catalyst surface. Special experiments have demonstrated that, in the absence of H_2S, the furan conversion on the alumina-supported catalysts at $T = 400°C$ and $\tau = 3.7$ s is negligible, but it increases upon the introduction of hydrogen sulfide into the system. Thiophene undergoes no conversion under these conditions. The postulated mechanism of thiophene formation from furan and H_2S differs from the mechanism suggested earlier for thiolation reactions of other oxygen-containing compounds. These reactions are assumed to proceed in steps, involving alkoxide structures and H_2S dissociatively chemisorbed on the surface, to yield HS^- groups and H^+ [1].

Earlier, we studied the reaction between furan and H_2S in the presence of a B/Al_2O_3 catalyst at T = 250–450°C, C_0 = 1–20 vol %, M = 0.4–20, and various contact times [17]. It was found that, at constant T, C_0, and M values, extending the contact time τ leads to an increase in the thiophene yield at a thiophene selectivity of 95–99% (Table 3). Varying the initial furan concentration at a constant M and τ has no effect on the furan conversion. As the initial H_2S concentration is maintained constant, the apparent rate constant of furan conversion (k_{fur}) is nearly invariable (Table 3, Fig. 3). The hydrogen sulfide conversion is independent of the initial H_2S concentration. At a constant C_0, the apparent rate constant of H_2S conversion (k_{HS}) is invariable (Table 4, Fig. 3). Therefore, the thiophene formation rate is first-order with respect to both furan and hydro-

Table 4. Effects of the initial H_2S concentration and the H_2S/furan ratio on thiophene synthesis at $T = 400°C$

τ, s	$[H_2S]_0$, vol %	C_0, vol %	M	X_{H_2S}, %	X_{fur}, %	k_{HS}, s^{-1}	k_{fur}, s^{-1}
2.0	7.2	20.5	0.4	11	7	0.06	0.05
1.9	8.0	1.0	8.0	9	85	0.05	1.0
2.0	9.2	1.3	7.1	12	78	0.06	0.8
2.0	9.8	1.4	7.0	10	86	0.05	1.0
1.7	10.7	1.6	6.9	14	73	0.09	0.8
2.0	24	8.7	2.8	13	40	0.07	0.3
1.9	37	13.3	2.7	10	32	0.05	0.2
1.75	46	10.0	4.6	–	50	–	0.4
2.0	49	11.8	4.1	8	46	0.04	0.3
1.9	64	20.0	3.2	10	32	0.06	0.2
2.0	80	4.1	20.0	–	98	–	2.0
2.0	92	8.3	11.0	11	88	0.06	1.1
0.8	9.9	1.6	6.1	10	43	0.13	0.7
2.4	9.4	1.5	7.0	15	88	0.07	0.9
1.1	79	4.3	18	7	87	0.07	1.9
2.0	57	7.8	7.3	8	90	0.04	1.15

Table 5. Furan conversion at various temperatures on the B/Al_2O_3 catalyst

T, °C	C_0, vol %	M	S, %	k_{fur}, s^{-1}*
250	1.80	6.7	100	0.06
300	1.40	6.8	98	0.26
350	1.43	6.8	98	0.34
400	1.56	6.9	97	0.70
420	1.56	6.0	96	0.83
450	1.60	6.2	95	0.96

* Activity was determined at $X = 50$–60% (at $T = 250$°C, $X = 32$%).

gen sulfide. It was found that the thiophene formation rate (productivity) at a constant initial furan concentration increases with an increasing H_2S/furan molar ratio (Fig. 4).

Raising the reaction temperature at a constant M causes an increase in the apparent rate constant of the reaction and reduces the thiophene selectivity from 100% at 250°C to 98–95% at 300–450°C (Table 5). A linear correlation is observed between the logarithm of the apparent first-order rate constant and reciprocal temperature (Fig. 5). The apparent activation energy is 38 ± 4 kJ/mol.

As the time on stream is extended from 1 to 1.5 h, the initial activity of the catalyst decreases by ~30% at a low H_2S concentration in the mixture and by 10–16% in the case of a large excess of H_2S over furan. Further extending the time on stream from 1.5 to 3 h has only a slight effect on the activity of the catalyst (Table 6). The deactivation of the catalyst is likely due to the fact that, in the sulfur-containing medium, the strongest acid sites on the catalyst surface are blocked and are thus excluded from participation in furan recyclization into thiophene [18].

Table 6. Stability data for the B/Al_2O_3 catalyst at $T = 400$°C and $\tau = 1.8$–2.0 s

Time on stream, min	$M = 4.2$–4.6		$M = 7.8$–8.1		$M = 10.9$–11.8	
	C_0, vol %	X/X_0^*	C_0, vol %	X/X_0^*	C_0, vol %	X/X_0^*
60	11.8	100	7.8	100	6.7	100
90	11.0	72	7.9	84	6.7	90
120	11.0	72	7.9	83	6.6	89
150	12.1	74	8.0	83	6.6	88
180	12.1	74	8.0	83	6.2	84

* Residual catalytic activity as the ratio of the furan conversion at a given time on stream to the furan conversion in the first hour.

Table 7. Activity of catalysts for thiophene synthesis from furan and H_2S

T, °C	Furan feed rate, mmol h^{-1} (g Cat)$^{-1}$	M	X, %	S, %	Thiophene formation rate, mmol h^{-1} (g Cat)$^{-1}$
$CoMo/Al_2O_3$, $P = 2.8$ MPa [8]					
250	0.42	12	87	88	0.32
350	2.32	12	100	78	1.80
280	2.32	12	43	81	0.37
$KPW/Al_2O_3^*$, $P = 0.95$ MPa [7]					
300	1.20	6	73	99	0.87
375	1.20	6	88	93	0.98
400	1.20	6	96	90	1.04
400	2.41	6	95	85	1.95
B/Al_2O_3, $P = 0.1$ MPa (this work)					
300	4.4	7	60	98	2.6
350	6.2	7	90	98	5.5
400	4.1	7	96	96	3.8
400	11.3	18	87	97	9.5
420	10.3	8	100	96	9.9
450	11.1	6	92	95	9.7

* KPW = potassium phosphotungstate.

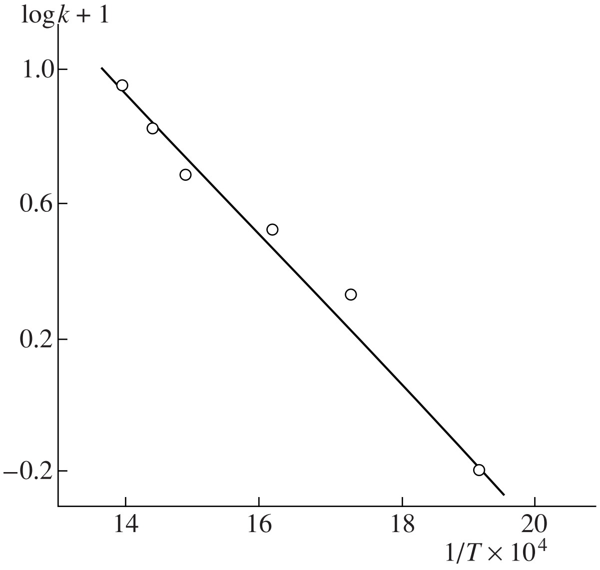


Fig. 5. Logarithm of the apparent rate constant of furan conversion versus reciprocal temperature (B/Al_2O_3 catalyst).

The data reported here can be used in developing a process for thiophene synthesis from furan and H_2S. It is appropriate to synthesize thiophene in the presence of the B/Al_2O_3 catalyst at atmospheric pressure, T = 300–400°C, C_0 = 12–14 vol %, and M = 6–7. Under these conditions, the thiophene yield is 95–98 mol % and the thiophene selectivity is 95–97%. As compared to patented data (Table 7), the thiophene formation rate with this catalyst is higher by a factor of 1.3–5.2.

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