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A Catalytic Process for Preparation of Thiophene from Furan and Hydrogen Sulfide

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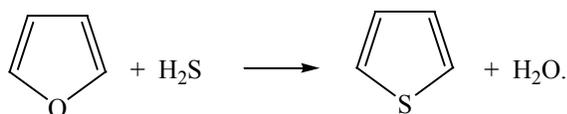
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Abstract—Thiophene formation under various conditions from furan and H₂S in the presence of γ -Al₂O₃, both unpromoted and promoted with transition metal oxides, was examined. The conditions enabling preparation of thiophene in a 95–98 mol% yield were determined.

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Thiophene is an important sulfur compound suitable for preparation of physiologically active substances, polymers, dyes, and oil additives [1]. It can be synthesized by various routes among which an important place belongs to that utilizing furan. The latter is produced in significant quantities from processing of pentosan-containing waste from agriculture, forestry, and woodworking [2]. It was found [3] that, in the presence of solid catalysts at atmospheric pressure and 300–600°C, furan reacts catalytically with H₂S to give thiophene:



In the presence of alumina, both unpromoted and promoted with Cr, Cu, and Th oxides, thiophene was obtained in a 20–37 mol% yield; the reaction is accompanied by the formation of abundant by-products responsible for the catalyst deactivation [3]. More recent studies [4–7] showed that, when catalyzed by promoted alumina, this reaction gives thiophene in a higher yield. The characteristics displayed in the reaction of thiophene synthesis from furan and hydrogen sulfide at atmospheric pressure and 400°C in the kinetic region were compared for catalysts of different nature, zeolites and SiO₂- and Al₂O₃-supported acids, alkalis, and metal oxides [7]. It was shown that the activity and selectivity of the catalysts is governed by the type, strength, and concentration of

the acid and basic sites on their surface and an important role played by Lewis acid sites (L-sites) was established. A mechanism was postulated according to which the reaction proceeds via formation of a surface intermediate through coordination of the α carbon atoms of the furan ring with the L-site and with the sulfur atom from the H₂S molecule nondissociatively adsorbed on the basic site (BS). The significance of the L-sites for the catalyst activity in the furan conversion to thiophene received further confirmation [8]. It was found that an increase in the Al₂O₃ precalcination temperature from 500 to 1300°C causes the concentration of the surface L-sites to decrease, thereby reducing the thiophene yield from 90 to 10%. The best performance in thiophene synthesis is exhibited by alumina-based catalysts [7]. However, the reaction catalyzed by them was not studied in detail; in particular, the activity of the catalysts was not examined in relation to the concentration of the transition metal oxide additions introduced into Al₂O₃.

Here, we measured in the kinetic region the activity and selectivity of Al₂O₃, both unpromoted and promoted with tungsten, molybdenum, chromium, and cobalt oxides. Our experiments demonstrated that unpromoted alumina performs better. In order to choose a catalyst best suited for practical application, we compared the Al₂O₃ samples differing in the specific surface area, pore structure, phase composition, catalyst grain size, and structural sodium content. For the most efficient catalyst

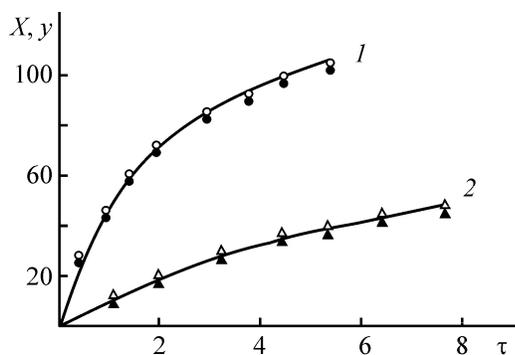


Fig. 1. (I) Degree of furan conversion X , %, and (II) thiophene yield y , %, at 400°C in the presence of catalysts with $d_{\text{grain}} = 0.25\text{--}0.5$ mm vs. contact time τ , s: (I) $\gamma\text{-Al}_2\text{O}_3$ and (2) $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$.

revealed, the kinetic relationships were examined, and the thiophene synthesis conditions were optimized.¹

EXPERIMENTAL

Hydrogen sulfide (99.5% pure) was prepared by the reaction of hydrogen with sulfur over an aluminum–nickel–molybdenum catalyst. We used pure-grade

Table 1. Thiophene formation from furan and hydrogen sulfide at 400°C in the presence of catalysts of different composition

Catalyst	τ , s	Thiophene yield, mol%	S , %
$\gamma\text{-Al}_2\text{O}_3$	1.0	45	100
	1.5	72	100
3% $\text{WO}_3/\gamma\text{-Al}_2\text{O}_3$	1.4	46	100
15% $\text{WO}_3/\gamma\text{-Al}_2\text{O}_3$	1.3	44	96
1.5% $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$	1.4	44	100
20% $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$	1.8	10	97
	8.0	42	90
0.5% $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$	1.3	36	98
2.3% $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$	1.3	12	96
	5.4	38	92
4% $\text{CoO}/\gamma\text{-Al}_2\text{O}_3$	1.5	35	97
10% $\text{CoO}/\gamma\text{-Al}_2\text{O}_3$	1.5	21	96

¹ The experimental part of work was carried out with partici-

furan; $\gamma\text{-Al}_2\text{O}_3$ with $S_{\text{sp}}=200$ m^2g^{-1} served as catalyst and support. The supported catalysts were prepared by impregnation of $\gamma\text{-Al}_2\text{O}_3$ having the grain size $d_{\text{grain}}=0.25\text{--}0.5$ mm with aqueous solutions of cobalt chloride, ammonium tungstate, ammonium molybdate, or chromium nitrate. The impregnated samples were dried, first in air at room temperature for 12 h and subsequently at 110°C for 5 h, after which they were calcined in a dry air stream at 500°C for 5 h. Also, we used commercial and prototype granular alumina samples as catalysts. The experiments were carried out in a flow reactor with a fixed bed of catalyst at atmospheric pressure. Helium from a cylinder was fed into a cooled saturator filled with furan. Helium-saturated furan was supplied to a mixer into which undiluted H_2S , or an H_2S –helium mixture, was supplied from another cylinder. The resulting gas mixture was fed into the heated reactor charged with the catalyst. The initial mixture and the reaction products were analyzed on an LKhM-8 MD chromatograph equipped with a katharometer [a $2\text{ m} \times 3\text{ mm}$ column packed with Porapak phase Q + R (1 : 1)]. The time of the experiment was 1 and 3.5 h in the case when the catalyst activity and the catalyst stability were determined, respectively.

The conditional contact time τ , s, was determined as the ratio of the catalyst volume to the gas flow rate, expressed in units of cubic centimeters and cubic centimeters per second, respectively, at atmospheric pressure and room temperature. Based on the results of the analysis we calculated the degree of reactant conversion X , %, thiophene yield y , mol%, selectivity with respect to thiophene S , %, $S = y/X$, and average rate of thiophene formation at $X = 50\%$ per catalyst gram w , $\text{mmol h}^{-1}\text{g}^{-1}$, which was taken as the measure of the catalyst activity.

In the presence of Al_2O_3 , both unpromoted and promoted with different amounts of transition metal oxides, in the kinetic region ($d_{\text{grain}}=0.25\text{--}0.5$ mm) we studied the reaction of H_2S with furan at atmospheric pressure, 400°C , initial furan concentration 1.5 ± 0.2 vol%, $\text{H}_2\text{S}/\text{furan}$ molar ratio $M = 6.5\text{--}7.0$, and different contact times. The main reaction product was thiophene, and minor amounts of carbon monoxide and ethylene by-products were obtained. Table 1 presents some of the results obtained. We found that, with all the catalysts examined, the degree of furan conversion and thiophene yield increased with increasing contact time (Fig. 1). For most of the catalysts examined these characteristics are virtually identical over a broad range of contact times, which suggests a close to 100% selectivity of thiophene formation. Table 1 shows that, at brief contact times ($\tau = 1.2\text{--}1.5$ s), unpromoted

γ -Al₂O₃ affords higher thiophene yield than does promoted γ -Al₂O₃. The activities of the γ -Al₂O₃ catalysts

containing relatively small amounts of reactive substances vary as follows:

Addition	Without addition	WO ₃	MoO ₃	Cr ₂ O ₃	CoO	H ₂ SO ₄	(NH ₄) ₂ WO ₄	Na ₂ O
<i>w</i> , mmol h ⁻¹ g ⁻¹	2.9	1.5	1.3	1.2	1.2	0.8	0.6	0.4

The catalysts containing W, Mo, Co, and Cr oxides are less active than unpromoted γ -Al₂O₃ by factors of 2 and over. For these catalysts an increase in the amount of addition caused the reaction to decelerate (Table 1).

The acid-base properties of alumina-based catalysts were examined previously using IR spectroscopy of adsorbed probe molecules [2, 9, 10]. On the γ -Al₂O₃ surface there are L-sites due to the presence of Al³⁺; their strength was estimated from the heat of adsorption of carbon monoxide Q_{CO} . Most of the sites have a moderate strength $Q_{CO}=34$ kJ mol⁻¹ in the concentration $c = 2.3$ μ mol m⁻²; also, there are strong L-sites with $Q_{CO} = 41$ kJ mol⁻¹, $c = 0.2$ μ mol m⁻². Basic sites contained in γ -Al₂O₃ in the concentration $c = 4$ μ mol m⁻² have a moderate strength of 800–900 kJ mol⁻¹, as estimated from the affinity of deuterium in CDCl₃ to the BS [9]. At high temperatures some of these sites are blocked by

H₂S, but their strength remains unchanged [11]. These sites on the γ -Al₂O₃ surface contribute to a high rate of furan conversion to thiophene. Adding small amounts of Mo, Cr, W, and Co oxides to γ -Al₂O₃ causes the strength of the L-sites from Al³⁺ to somewhat increase ($Q_{CO} = 36$ – 37 kJ mol⁻¹), and the strength of the BS sites varies only slightly. However, at a high content of these additions in the catalyst the L-sites are represented mostly by transition metal cations whose Lewis acidity is lower than that of Al³⁺ [9], which leads to decreased activity of the catalyst in thiophene formation. Our data suggest that, in the reaction of thiophene synthesis from furan and hydrogen sulfide, unpromoted γ -Al₂O₃ comprising strong L-sites and moderately strong BSs performs better than does promoted alumina. The catalytic properties of alumina can be affected by various factors: phase composition, pore structure,

Table 2. Influence of the nature of alumina on its activity in thiophene synthesis

Phase composition of Al ₂ O ₃	Shape	Grain size, mm	S_{sp} , m ² g ⁻¹	Na, wt%	V_{pore} at $R = 70$ – 100 nm	w , ^a mmol h ⁻¹ g ⁻¹
γ -Al ₂ O ₃	Spherical	4–5	350	0.03	0.08	1.3
	"	4–5	350	0.10	0.08	1.0
	"	2–3	350	0.03	0.08	1.4
	"	0.25–0.5	350	0.03	0.08	1.8
	Rod-like	3–4	220	0.03	0.07	0.7
	"	3–4	210	0.03	0.04	0.6
	"	2–3	210	0.02	0.07	1.0
	"	4–5	200	0.02	0.34	1.1
50% γ -Al ₂ O ₃ + 50% χ -Al ₂ O ₃	Spherical	0.25–0.5	200	0.02	0.34	1.2
	"	4–5	345	0.06	0.12	0.9
50% γ -Al ₂ O ₃ + 40% χ -Al ₂ O ₃ + 10% η -Al ₂ O ₃	"	4–5	350	0.07	0.05	0.4

^a The activity of whole catalyst grains was measured at 400°C, furan concentration ~2%, $M = 5.2$ – 5.5 , and $X = 60$ – 70% .

specific surface area, grain size, and structural sodium (Na incorporated into the γ - Al_2O_3 lattice) impurity content. Therefore, we examined a series of alumina catalysts with different parameters. Table 2 summarizes the results obtained.

It is seen that, with decreasing grain size, the activity of alumina tends to increase. With the transport pore volume and structural sodium impurity content being identical, the reaction rate tends to increase proportionally to increase in the specific surface area of the catalyst. The catalyst comprised of γ - Al_2O_3 and χ - Al_2O_3 exhibits a lower activity; the catalyst based on $(\gamma + \chi + \eta)$ - Al_2O_3 , which moreover has a small volume of transport pores, is even less active.

Heterogeneous catalytic processes are typically complicated by diffusion phenomena [12]. It was shown experimentally that the observed rate of thiophene formation from furan and hydrogen sulfide is independent of the gas velocities no lower than 0.8 l h^{-1} . Also, the reaction is substantially accelerated with increasing temperature. Apparently, there is no significant external diffusion inhibition. The specific surface area and pore structure of the catalyst affect the reaction rate, which fact may be indicative of internal diffusion complications. The degree of utilization of the surface of whole catalyst grains is

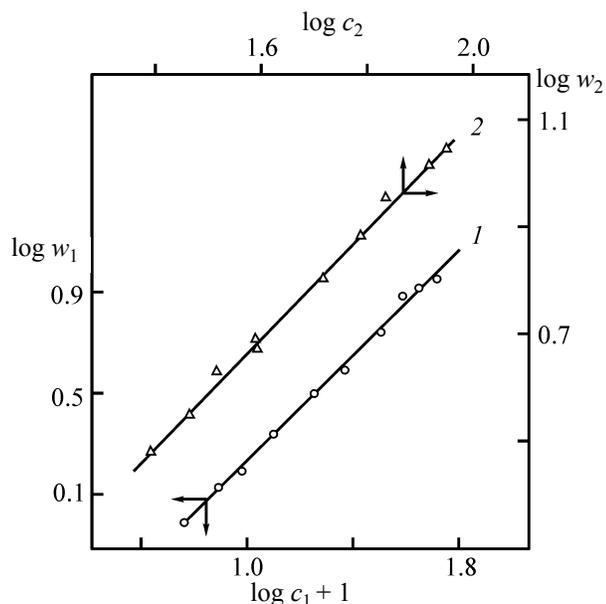


Fig. 2. (1) Furan conversion rate w_1 vs. running furan concentration c_1 at the initial H_2S concentration of 10–11 vol% and (2) hydrogen sulfide conversion rate w_2 vs. running H_2S concentration c_2 at the initial furan concentration of 12–13 vol%.

estimated from the ratio of the observed reaction rate to the rate achieved under presumption of the accessibility of the entire inner surface of the catalyst for the reactants and products [12].

We carried out experiments with γ - Al_2O_3 samples characterized by various crushing degrees and found that the reaction rate is unaffected by a decrease in the grain size beyond 0.25–0.5 mm. Therefore, the degree of the surface utilization was estimated from the ratio of the reaction rates on the whole grains and grains with a size of 0.25–0.5 mm. We found that surface is utilized nearly exhaustively at the transport pore volume of $0.34 \text{ cm}^3 \text{ g}^{-1}$, below which level the degree of the surface utilization does not exceed 0.7–0.8. The process parameters were examined in relation to the reaction conditions in the presence of γ - Al_2O_3 with $S_{\text{sp}} = 330 \text{ m}^2 \text{ g}^{-1}$, Na content 0.03 wt%, and $d_{\text{grain}} = 0.25\text{--}0.5 \text{ mm}$ in the kinetic region. The experiments were carried out at atmospheric pressure, temperature 250–480°C, initial furan concentration 1–20 vol%, H_2S concentration 9–60 vol%, $M = 2.8\text{--}20$, and different contact times. Table 3 and Fig. 2 present the results obtained.

It is seen that, when the temperature and initial concentrations of the reactants are constant, the degree of furan conversion and thiophene yield tend to increase with increasing contact time; the selectivity of thiophene formation is 97–100%. When the contact time and H_2S /furan molar ratio remain constant, the degree of furan conversion and thiophene yield are virtually unaffected by an increase in the initial furan concentration. At a constant H_2S concentration the reaction rate tends to increase in direct proportion to the running concentration of furan, and at a constant furan concentration it also increases in direct proportion to increase in the running concentration of H_2S . The reaction is described by a first-order equation with respect to both furan and hydrogen sulfide. When the temperature and initial concentration of furan are kept constant, an increase in M from 1 to 16 causes the thiophene formation rate to increase by nearly an order of magnitude. For example, at 400°C and furan concentration of 2 vol% we obtained the following results:

$\text{H}_2\text{S}/\text{furan}$	1.0	3.1	4.5	6.2	8.5	11.2	16.0
$w, \text{ mmol h}^{-1} \text{ g}^{-1}$	0.4	1.0	1.4	1.6	2.0	2.7	3.6

An increase in temperature leads not only to acceleration of the thiophene formation but also to a certain

decrease in selectivity. Given below are the data obtained at the initial furan concentration of 1.5 vol% and $M = 7$:

$T_{\text{exp}}, ^\circ\text{C}$	250	300	350	400	420	450	480
$w, \text{mmol h}^{-1} \text{g}^{-1}$	0.2	0.6	0.8	1.6	1.8	2.2	2.7
$S, \%$	100	99	97	96	96	95	94

The experiments aimed to determine the stability of the catalyst showed that the relative rate of thiophene formation w/w_0 , where w_0 and w are the thiophene formation rates in the initial period and during the experiment, respectively, increases in the case when H_2S is taken in a large excess over furan (Fig. 3).

Our data suggest that synthesis of thiophene from furan and H_2S is to be catalyzed by $\gamma\text{-Al}_2\text{O}_3$ unpromoted with metal oxides, having the following characteristics: grain size ~ 3 mm, specific surface area $\geq 330 \text{ m}^2 \text{ g}^{-1}$, structural sodium content $< 0.05 \text{ wt}\%$, and the specific volume of transport pores $\geq 0.08 \text{ cm}^3 \text{ g}^{-1}$.

As follows from our calculations, thiophene can be synthesized from furan and hydrogen sulfide in an adiabatic fixed-bed reactor with alumina having grain size ~ 3 mm at atmospheric pressure, temperature $400\text{--}450^\circ\text{C}$, furan supply rate $0.3\text{--}0.7 \text{ kg h}^{-1} \text{ kg}^{-1}$, furan initial concentration $12\text{--}14 \text{ vol}\%$, and $\text{H}_2\text{S}/\text{furan}$ molar ratio $4\text{--}5$. Under the recommended conditions the thiophene yield is $95\text{--}98 \text{ mol}\%$. This process is more efficient than the known processes employed for thiophene preparation by the reaction of furan with hydrogen sulfide [4–6], catalyzed by promoted alumina.

CONCLUSIONS

(1) The highest activity in thiophene synthesis from furan and hydrogen sulfide at atmospheric pressure is exhibited by unpromoted $\gamma\text{-Al}_2\text{O}_3$ containing strong L-sites and basic sites of moderate strength.

(2) The activity of $\gamma\text{-Al}_2\text{O}_3$ tends to increase with increasing catalyst surface area and transport pore volume, as well as with decreasing grain size; it decreases in the presence of χ - and η -phases, along with γ -phase, in alumina and at a high content of structural sodium.

(3) The reaction of furan with hydrogen sulfide over $\gamma\text{-Al}_2\text{O}_3$, is described by a first-order order equation with respect to furan and hydrogen sulfide; the thiophene formation is accelerated with increasing $\text{H}_2\text{S}/\text{furan}$

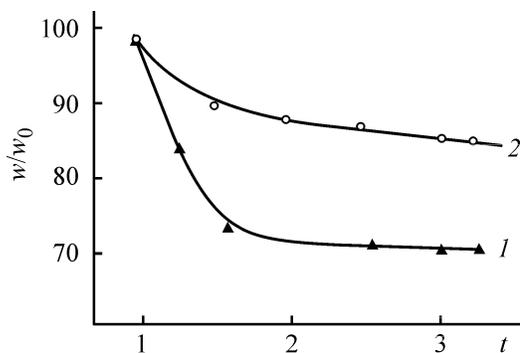


Fig. 3. Initial rate of thiophene formation vs. experiment time t , h. Catalyst $\gamma\text{-Al}_2\text{O}_3$, $\tau = 1.8\text{--}2.0$ s. (w/w_0) Rate ratio, %. M : (1) 4–5 and (2) 2.

Table 3. Furan conversion in an H_2S medium at 400°C in the presence of granular $\gamma\text{-Al}_2\text{O}_3$

τ, s	Initial concentration, vol%		$\text{H}_2\text{S}/\text{furan}$	Thiophene yield, mol%	Selectivity with respect to thiophene, %
	furan	H_2S			
0.6	1.4	9.7	7.1	23	96
1.2	1.7	10.7	6.3	46	100
1.6	1.6	11.3	7.0	57	98
2.4	1.5	10.2	6.8	71	97
2.6	1.6	11.4	7.1	75	99
3.0	1.4	9.8	7.0	82	98
3.9	1.7	11.4	6.7	95	99
1.5	4.4	79	18	83	98
2.5	4.0	80	20	94	97
2.5	1.2	9.2	7.6	78	96
2.4	1.7	12	7.1	77	97
2.6	5.0	34	6.9	76	98
2.8	8.6	26	3.0	38	96
2.5	8.2	82	10	82	97
2.4	13	36	2.8	28	98
2.6	12	52	4.3	46	97
2.4	20	60	3.0	30	96

molar ratio and temperature rising from 250 to 480°C.

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