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Catalytic methods of synthesis of thiophenes from hydrocarbons and hydrogen sulfide

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Abstract. The synthesis of thiophene and alkylthiophenes by the reaction of acetylene, C_4-C_8 alkanes, and C_4-C_6 alkenes and alkadienes with hydrogen sulfide in the presence of metal oxides and sulfides as well as their mixtures is examined. The conditions for the testing of catalysts in flow type apparatus in stationary and fluidised catalyst beds are presented. The calculated equilibrium yields of thiophenes from C_4-C_6 hydrocarbons and hydrogen sulfide are compared with experimental data. Together with the heterocyclisation reaction, the interaction of C_6-C_8 hydrocarbons with hydrogen sulfide involves dehydrocyclisation with formation of aromatic hydrocarbons. The mechanism of the interaction of C_4-C_5 hydrocarbons with hydrogen sulfide, investigated by the isotope-kinetic method, is discussed. Certain physicochemical properties of active chromium-containing oxide heterocyclisation catalysts and industrial methods of synthesis of thiophene are described. The bibliography includes 63 references.

I. Introduction

During the 1960s, information concerning the selection of effective catalysts for the synthesis of thiophene and alkylthiophenes by the heterocyclisation reaction was available, with some exceptions, only in the patent literature. Transition metal oxides and sulfides were used as the catalysts.

A review of catalytic methods of synthesis of thiophene and alkylthiophenes from petroleum processing products and organic sulfur-containing compounds was published in 1971.[1] Analysis of the review data leads to the conclusion that it is most useful to obtain thiophenes from readily available starting materials — hydrocarbons and hydrogen sulfide. The selection of an effective catalyst capable of being regenerated would make such a process promising. The use of sulfur-containing organic compounds is difficult in practice because dialkyl sulfides, mercaptans, and thiophane are not yet produced on an industrial scale.

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By virtue of their high reactivity, thiophene and its homologues are a potential starting material for the synthesis of a wide variety of both aliphatic and alicyclic compounds. Methods of synthesis of certain polyorganosiloxanes, herbicides, physiologically active substances, and perfumes from thiophene have been developed. The successful development of thiophene chemistry, especially during the last ten years, has made it possible to develop a series of valuable medicinal preparations, including antibiotics. Like benzene, thiophene is known to possess biological activity but it is less toxic. Compounds containing thiophene and its derivatives can be used in the treatment of diseases of the central nervous system and also as anti-inflammatory, cardiovascular, antihistamine, and other agents.

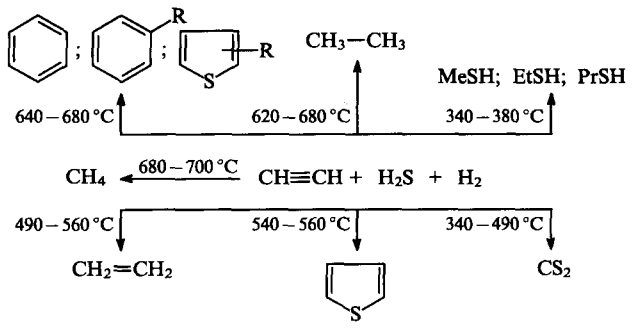
The literature data on thiophene and its derivatives published up to 1982 have been surveyed in a monograph[2] which was published in 1985. The methods of synthesis of thiophene by a cyclisation reaction and from other cyclic systems are described in the monograph and the pharmacological activity of thiophene and its derivatives have also been considered.[3,4]

II. Interaction of acetylene with hydrogen sulfide

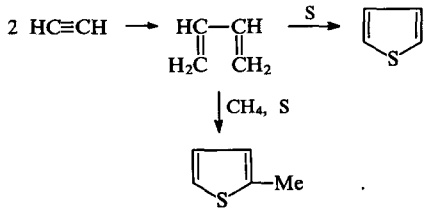
Thiophene was first obtained from acetylene and hydrogen sulfide by Chichibabin in 1915.[5] The reaction was carried out in the presence of aluminium oxide at 425–450 °C. The studies on the catalytic synthesis of thiophene from hydrogen sulfide and acetylene up to 1952 have been surveyed in a monograph.[6]

Interesting results have been obtained[7,8] in experiments on γ-Al_2O_3 in the study of the interaction of hydrogen sulfide and an acetylene-containing gas from the electrocracking of petroleum products, the gas having the following composition (vol.%): 29.0 C_2H_2, 7.8 C_2H_4, 0.6 C_2H_6, 5.6 CH_4, and 57.0 H_2. The yield of thiophene proved to be higher than in the case where pure acetylene was used and amounted to 50%–52% relative to the acetylene passed through the system instead of 38%. The high activity at γ-Al_2O_3 is probably associated with the presence of hydrogen in the initial mixture, which promotes hydrogenation and the removal of carbonaceous deposits — the condensation products on the surface of alumina.

Depending on the temperature, the following products are obtained in the interaction of the acetylene-containing electrocracking gas with hydrogen sulfide on γ-Al_2O_3:



The introduction of transition metal (Cr, La) oxides as well as K_2O intensifies the hydrogenating function of the catalyst—the yield of ethylene and ethane increases by a factor of 1.5, but the yield of thiophene does not increase. These data, as well as the results of experiments in which a mixture of 30% of ethylene with H_2S was used, show that thiophene is not formed via hydrogenation products. It is most likely that the formation of thiophenes and alkylthiophenes involves the intermediate formation of dimerisation and alkylation products in accordance with the mechanism[9]



The yield of thiophene on γ-Al_2O_3 did not change with increase in the rate of supply of acetylene.[10] The size of the catalyst grains also did not affect the yield of thiophene. The concentration of the helium-diluted hydrogen sulfide was varied from 0 to 87.5 mass% at an acetylene concentration of 12.5 mass%. The activation energy for the synthesis of thiophene from hydrogen sulfide and acetylene at 300–400 °C was 153 kJ mol^{-1}.[10] The reaction is influenced by the surface acidity of γ-Al_2O_3. The presence on the catalyst surface of weak acid centres, probably electron-accepting, is necessary for the formation of thiophene. Strong proton centres promote appreciable coke formation, which results in a rapid loss of activity by the catalyst.[11]

In the search for a possible increase in the activity of γ-Al_2O_3 in the temperature range 350–450 °C, a study was made of the influence of La, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn oxides.[12] Catalysts containing 0.5–2.5 mass% of Cr, Co, and Ni oxides showed the highest activity. In terms of their activity in the formation of thiophene from acetylene and hydrogen sulfide, the catalysts can be arranged in the sequence Cr_2O_3, Al_2O_3 > Co_3O_4, Al_2O_3 > NiO, Al_2O_3 > Al_2O_3. An increase in the content of the additives leads to an increase in the rate of formation of side products, in particular of the condensation of acetylene. The introduction of promoting oxides increases the activity of γ-Al_2O_3 in reactions involving the elimination of hydrogen from ethanethiol and the redistribution of hydrogen, the catalyst with added Cr_2O_3 showing the highest activity.

The dependence of the activity of a two-component catalyst on the structure of the *d* electron shell of the constituent ions has two peaks.[12] The Al, Cr and Al, Co catalysts show the maximum activity, their ions having the d^3, d^6, and d^7 electronic configurations. The introduction of ions with the d^8, d^9, and d^{10} electron shells probably hinders the activation of hydrogen sulfide molecules, which do not tend to form a dative bond, and enhances the activation of acetylene molecules, which increases the rate of formation of high-molecular-mass products on the catalyst surface. The low activity of the catalyst containing Ti^{4+} and Fe^{3+} has been explained[12] in terms of the zero stabilisation energy of ions with d^0 and d^5 configurations.

When the acetylene–hydrogen mixture containing 30 vol.% of acetylene was used (490–500 °C, space velocity v_{sp} = 300 to 320 h^{-1} with respect to acetylene, and H_2S : C_2H_2 = 1), thiophene was obtained on γ-Al_2O_3 in 16.4% yield.[13] The introduction of chromium oxide into aluminium oxide increased the rate of heterocyclisation: the yield of thiophene increased by a factor of 1.6. At the same time, the content of acetylene rose by a factor of 10 and that of ethane by a factor of 2. Under these conditions, the amount of coke diminished by a factor of 2. The dimerising effect of the aluminium oxide–chromium oxide catalyst was manifested by an increase in the yield of C_4 hydrocarbons by a factor of almost 2. The addition of lanthanum and potassium oxides to the aluminium oxide–chromium oxide catalyst increased the hydrogenating activity and diminished coke formation. The highest yield (26.3%) of thiophene from the acetylene–hydrogen mixture was obtained in the presence of the 5% Cr_2O_3–95% γ-Al_2O_3 catalyst.[13]

III. Interaction of C_4 hydrocarbons with hydrogen sulfide

Thiophene has been obtained mainly from C_4 olefins and hydrogen sulfide over various catalysts containing chromium or molybdenum oxides on aluminium oxide, bauxite, or silica gel.[1] The reaction is slightly endothermic and can be carried out in a flow system. However, the catalyst requires periodic regeneration with air. Since this entails a large exothermic effect and an increase in temperature, it is more convenient to employ a catalyst in a fluidised bed. This diminishes the temperature rise during regeneration.

Thiophene has been obtained in a high yield from hydrogen sulfide and n-C_4 hydrocarbons.[14] The yield of thiophene from butenes is higher than from n-butane. Thus the yields of thiophene were 31.2%, 52.9%, and 55.4% from butane, but-1-ene, and but-2-ene respectively in the presence of the 5% SiO_2–10% MoO_3–85% Al_2O_3 catalyst (590 °C, H_2S : hydrocarbon = 1.6 : 1.8, v_{sp} = 1.5–1.7 h^{-1}).

An effective aluminium oxide–chromium oxide catalyst with oxide additives was selected for the reaction of butane, butene, or butadiene with hydrogen sulfide.[16] It was shown[15,16] that the γ-Al_2O_3 carrier exhibits mainly a cracking activity and a weak heterocyclising activity, whereas chromium oxide exhibits dehydrogenating, hydrogenating, heterocyclising, and cracking properties. The following reactions take place on the aluminium oxide–chromium oxide catalyst when butane interacts with hydrogen sulfide: heterocyclisation with formation of thiophene, dehydrogenation with formation of alkenes and alkadienes, cracking with formation of C_1–C_3 hydrocarbons, and coke formation. By introducing the lanthanum oxide[15] and potassium oxide[16] additives into the aluminium oxide–chromium oxide catalyst, it is possible to increase its heterocyclising and dehydrogenating activities and to weaken its cracking and coke forming functions. Potassium oxide also increases the stability of the catalyst. By selecting the concentrations of the components, the optimum composition of the polyfunctional catalyst (mass%) was found: 5 Cr_2O_3, 5 La_2O_3, 1 K_2O, and 89 γ-Al_2O_3.[16] The introduction of lanthanum and potassium oxides into the aluminium oxide–chromium oxide catalyst increased the yield of thiophene by a factor of 1.4–1.75 and diminished the formation of C_1–C_3 hydrocarbons by a factor of 1.2–1.5 and the deposition of coke by a factor of 1.5–2.8 (Table 1).

It has been shown that the heterocyclisation, dehydrogenation, and cracking reactions proceed on the same catalyst active centres. The cracking functions can be suppressed to a slight extent by introducing alkaline additives.[17] Under optimum conditions in the interaction of C_4 hydrocarbons with hydrogen sulfide in the presence of the catalyst comprising chromium, lanthanum, potassium, and aluminium oxides, thiophene was formed in

Table 1. The interaction of hydrogen sulfide with C_4 hydrocarbons in the presence of chromium-containing catalysts (according to the data of Ryashentseva et al.[18]).

Initial hydrocarbon	Catalyst mass%	T/°C	Yield relative to C_4 passed through system (%)				
			of thiophene (rel to theoretical)	C_1-C_3	C_4H_8	C_4H_{10}	coke
Butane	5 Cr_2O_3, 95 Al_2O_3	580	12.5	45.7	8.3	–	3.3
	5 Cr_2O_3, 5 La_2O_3, 1 K_2O, 89 Al_2O_3	580	21.8	39.7	11.0	–	1.3
But-1-ene	5 Cr_2O_3, 95 Al_2O_3	500	21.7	31.2	–	6.0	6.5
	5 Cr_2O_3, 5 La_2O_3, 1 K_2O, 89 Al_2O_3	500	37.9	20.4	–	8.0	2.3
Butadiene	5 Cr_2O_3, 95 Al_2O_3	500	21.9	13.9	27.1	9.2	6.4
	5 Cr_2O_3, 5 La_2O_3, 1 K_2O, 89 Al_2O_3	500	30.6	9.2	27.1	8.9	4.2

40%–55% yield relative to the hydrocarbon passed through the system. Under conditions where this catalyst was used continuously, the yield of thiophene from butane and hydrogen sulfide fell from 37%–40% in the first 2–3 h to 23% in the next 7 h. The conditions for the regeneration of the catalyst after its use for 1, 2, and 3 h were found; the regeneration time is equal to the contact time.[17,18]

Thermodynamic calculations for the reactions involving the formation of thiophene from n-butane, but-1-ene, *cis*- and *trans*-but-2-enes, buta-1,3-diene, and hydrogen sulfide, taking into account the extent of side reactions,[19] made it possible to determine the equilibrium constants for these reactions in the temperature range 300–1000 K and also to calculate the equilibrium yields of thiophene for the stoichiometric and excess amounts of hydrogen sulfide relative to the hydrocarbon at 700–900 K. In order to compare the experimental and calculated equilibrium yields of thiophene in the presence of the Cr, La, K, Al catalyst, experiments were performed with [the determination] of the material balance of the products of the interaction of C_4 hydrocarbons and hydrogen sulfide. The experimental yields of thiophene obtained by the reaction of butane, but-1-ene, and buta-1,3-diene with hydrogen sulfide were 60%, 70%, and 90% respectively relative to the calculated equilibrium yield (taking into account side reactions).[19]

Certain data concerning the synthesis of thiophene from alkenes and alkadienes have been published in Japanese patents.[20,21] In the presence of the 12 Cr_2O_3–5 K_2O–83 Al_2O_3 catalyst (compositions in mass%) at 500 °C and for a contact time of 8.8 s, 26% of thiophene was formed from but-1-ene and hydrogen sulfide in the presence of nitrogen (molar ratios 1 : 2 : 4).[20] In the presence of the V_2O_5–Al_2O_3 catalyst at 410 °C, 49.7% of thiophene was obtained from buta-1,3-diene and hydrogen sulfide.[21]

The interaction of hydrogen sulfide with a butane–butene fraction (BBF) having the composition (mass%) 0.9 C_2-C_3, 11.3 iso-C_4H_8, 22.9 n-C_4H_8, 40.5 iso-C_4H_{10}, 23.2 n-C_4H_{10}, and 1.2 C_5 hydrocarbons has been investigated.[22] The reaction was carried out in a reactor with a vibrofluidised bed of a catalyst comprising Cr, La, K, and Al oxides (Cr, La, K, Al catalyst) at temperatures in the range 400–600 °C, with v_{sp} = 100–700 h^{-1}, and for the component ratio H_2S : BBF = (0.5–5.0) : 1. The yield of thiophene was higher than in the reactor with a stationary catalyst bed. The use of a gradient-free reactor with forced fluidisation facilitates the measurement of the rate of reaction in the initial instants of the employment of the catalyst, which is particularly important when catalysts with a variable activity are used.[22]

The synthesis of thiophene in the presence of a catalyst in which lanthanum oxide has been replaced by a mixture of lanthanide oxides may be of interest from the practical point of view. In the presence of the catalyst having the composition (mass%) 5 Cr_2O_3, 1 K_2O, 5 Ln (2.7 CeO_2, 1.3 La_2O_3, 0.75 Nd_2O_3, and 0.25 Pr_6O_{11}), and 89 Al_2O_3, the interaction of hydrogen sulfide with BBF was investigated and it was shown that the effectiveness of the reaction in a vibrofluidised bed is higher than in a stationary bed.[23,24] The corresponding data are presented in Table 2.

Table 2. The interaction of hydrogen sulfide with the butane–butene fraction (BBF) over the Cr, Ln, K, Al catalyst (according to the data of Abramovich et al.[24]).

T/°C	v_{sp}/h^{-1}	H_2S : BBF (mol.%)	Yield of thiophene[a] relative to			
			n-butane		BBF	
			A	B	A	B
520	200	1.4	–	41.6	32.5	55.4
545	243	2.2	27.7[b]	75.0	–	–
562	128	1.7	–	84.1	44.8	71.7
565	123	2.7	–	88.1	–	–
580	153	2.7	66.8	–	46.2	76.8
595	216	2.2	49.7[b]	91.2	57.7	89.1
610	152	1.7	38.0	–	46.2	76.8
614	145	3.0	–	83.7	–	–

[a] A—in a stationary bed, B—in a vibrofluidised bed.
[b] For v_{sp} = 229 h^{-1}.

The best yield of thiophene (66.8% relative to the hydrocarbon passed through the system) in a stationary catalyst bed was achieved at 580 °C for v_{sp} = 153 h^{-1} and H_2S : BBF = 2.7. The yield of thiophene falls with increase in temperature. In a reactor with a vibrofluidised bed under similar conditions (595 °C, v_{sp} = 216–228 h^{-1}, H_2S : BBF = 2–2.2), the yield of thiophene reached 91.2% relative to n-butane passed through the system or 89.1% relative to BBF. Above 600 °C, the yield of thiophene in both stationary and vibrofluidised beds diminishes, which is apparently associated with the decomposition of the initial hydrocarbon. Gradient-free conditions with respect to temperature are achieved in a reactor with a vibrofluidised bed; the reaction takes place under isothermal conditions, where a higher equilibrium degree of conversion and lower equilibrium concentrations of the initial hydrocarbons than under adiabatic conditions are attained.[24]

The influence of modifying additives on the heterocyclising activity of the aluminium oxide–chromium oxide catalyst has been investigated in the reaction of BBF with hydrogen sulfide. Li, K, Rb, Cs, Sr, Cd, Be, Se, Ti, and Mo oxides were used as additives.[25] The content of butane and butene in the industrial BBF was 40%–50%. The reaction was carried out at 570–590 °C, at a space velocity of 100–500 h^{-1}, for a molar ratio H_2S : BBF = (1.5–3.0) : 1, and with a duration of the experiment of 60 min. The replacement of potassium oxide by lithium, rubidium and caesium oxides proved ineffective: the yield

of thiophene was appreciably lower than in the presence of the Cr, K, Al catalyst. The yield of thiophene relative to the n-C_4 hydrocarbon passed through the system in the presence of the Cr, K, Al catalyst promoted with selenium dioxide was 85.4%. Among lanthanide oxides, those of scandium, praseodymium, and gadolinium as well as that of indium proved to be the most effective promoting agents. Catalysts with added samarium and cerium oxides are of special interest, the yield of thiophene in the presence of the latter attaining 85%–90%. In order to carry out the reaction in a fluidised catalyst bed, the mechanically strong γ-Al_2O_3 in the form of spherical pellets was employed. In the presence of the catalysts (the compositions are in mass%), 15.5 Cr_2O_3 – 1.9 K_2O – 4.5 In_2O_3 – 78.1 γ-Al_2O_3 and 14.8 Cr_2O_3 – 2.0 K_2O – 4.9 Sm_2O_3 – 78.3 Al_2O_3, the yields of thiophene (relative to the n-C_4 hydrocarbon passed through the system) were 71.6% and 66.0% respectively. However, the activity of these catalysts was not higher than that of the Cr, K, Ln, Al catalyst.[24]

When a zeolite was used as a carrier, the chromium catalysts had a low activity in the reaction of BBF with H_2S.[25] Catalysts based on type A zeolites in both the sodium- and calcium-forms proved to be completely inactive. The low activity of the chromium oxide–zeolite catalyst can be accounted for by the discrepancy between the dimensions of the window-channels and the dimensions of the molecules of the initial compounds and products.

Thiophene has also been obtained on sulfide catalysts. The properties of the aluminorhenium sulfide [aluminium sulfide–rhenium sulfide?] catalysts have been investigated in relation to the reaction of n-butane with hydrogen sulfide.[26] Rhenium sulfide Re_2S_7 has a high catalytic activity, for example in the hydrogenation of sulfur- and nitrogen-containing heterocyclic compounds.[27] In contrast to the chromium-containing Cr, La, K, Al and Cr, Ln, K, Al catalysts, carbon disulfide (12%) was obtained together with thiophene (14%) in the presence of a H_2S-treated catalyst comprising 11% Re and 89% γ-Al_2O_3 [580 °C, v_{sp} = 250 h^{-1}, H_2S : n-C_4 = (3–5) : 1]. The formation of carbon disulfide can be explained by the interaction of sulfur with the carbon produced as a result of the cracking of the hydrocarbons on the catalyst. The source of sulfur may be both the surface of the sulfided catalyst and the decomposition of hydrogen sulfide under the catalytic conditions. This is confirmed by the increase to 24% of the yield of carbon disulfide with increase in the molar ratio of H_2S and n-butane to 9. The yield of thiophene also increases under these conditions (to 21%). These data indicate indirectly the formation of thiophene and carbon disulfide on the same catalyst active centres.

A multistage mechanism has been proposed for the formation of thiophene from butadiene and hydrogen sulfide in the presence of sulfide catalysts.[28] It is postulated that butadiene interacts with the surface sulfur in the slow stage. This is followed by the resulfidation of the catalyst by the sulfur from the reaction medium and the restoration of the stationary composition of the surface. Sulfided Cr and Mo oxides as well as Re_2S_7 were used as the catalyst. The activity of the catalyst was determined by a pulse method at 400–500 °C for a contact time of 1.2–3 s using helium as the diluent gas. It was postulated that the surface becomes coated with sulfur as a result of the treatment of the catalyst with hydrogen sulfide before the start of the experiment. The resulfidation stage is not rate-limiting, the removal of sulfur from the surface by butadiene with formation of thiophene occurring most slowly. The most active catalysts contain sulfur weakly bound to the surface.[28]

IV. Interaction of C_5 hydrocarbons with hydrogen sulfide

There exist patent data concerning the synthesis of alkylthiophenes by the reaction of C_5 alkadienes with hydrogen sulfide in the presence of aluminium oxide–chromium oxide catalysts.[5] Various multicomponent catalysts have been compared in the synthesis of 2-methylthiophene by the reaction of piperylene with hydrogen sulfide.[29] Under optimum conditions [480–500 °C, v_{sp} = 0.5–0.7 h^{-1}, H_2S : C_5 = (2–4) : 1], the yield of 2-methylthiophene in the presence of the Cr, K, Al catalyst was 35 to 40 mass%. The catalyst was regenerated with a 1 : 1 air–nitrogen mixture in order to remove coke, after which it was exposed to a stream of hydrogen.[30] The catalytic activity increases with increase in the temperature of the preliminary treatment of the catalyst with hydrogen up to 600 °C and at a space velocity up to 200 h^{-1}. The effect obtained has been explained by the enhancement of the desorption of water formed as a result of the reduction of Cr^{6+} by hydrogen.[31]

Preliminary treatment of the Cr, K, Al catalyst with hydrogen sulfide increases its activity and selectivity as a consequence of the interaction of sulfur with the surface.[32] In order to elucidate the nature of the bond between sulfur and the catalyst [Cat(S)], the latter was treated with hydrogen sulfide for 5–90 min at 200–500 °C and a space velocity of 600–700 h^{-1}. The influence of this treatment on the activity of the catalyst was estimated from the yield of 2-methylthiophene from H_2S and piperylene at 500 °C, v_{sp} = 2.7 h^{-1}, and H_2S : C_5 = 2.1–2.2.[33] The kinetic model of the process can be described by the equations presented in Scheme 1.

Scheme 1

$$H_2S \rightleftharpoons H_2 + S \quad (1)$$

$$Cat(S)S + C_5H_8 \longrightarrow C_5H_6S + H_2 + CatS \quad (2)$$

$$C_5H_8 \longrightarrow \text{coke} \quad (3)$$

$$C_5H_6S \longrightarrow \text{coke} \quad (4)$$

$$C_5H_8 \longrightarrow \text{gas} \quad (5)$$

Hydrogen sulfide dissociates in the first stage at a temperature above 400 °C. This is confirmed by the fact that treatment of the catalyst surface with hydrogen sulfide at lower temperatures does not increase the activity of the catalyst. Thiophene is formed mainly as a result of the interaction of piperylene with the sulfur chemisorbed on the sulfided catalyst.[33]

In the presence of an effective catalyst having the composition (mass%)[34] 18 Cr_2O_3, 4 K_2O, and 78 Al_2O_3 under optimum conditions [470–500 °C, v_{sp} = 0.5–0.7 h^{-1}, H_2S : C_5 = (2–1) : 1], 2-methylthiophene was obtained from hydrogen sulfide and piperylene in 62% yield, while 3-methylthiophene was obtained from 2-methylbut-2-ene and hydrogen sulfide in 75% yield.[29–33] 3-Methylthiophene was obtained in 53% yield from isoprene and hydrogen sulfide at 500 °C and a gas flow rate v_{mass} = 0.34 h^{-1} [H_2S : C_5 = (4–5) : 1] in the presence of a catalyst having the composition (mass%) 5 Cr_2O_3, 5 La_2O_3, 1 K_2O, and 89 Al_2O_3.[16] 2-Methylthiophene was obtained in 43.2% yield from piperylene and hydrogen sulfide under the same conditions.[17] It has been stated that aluminium oxide (77.5 mass%–78.5 mass%) with a specific surface of 150 to 170 m^2 g^{-1} is used to increase the activity and mechanical strength of the catalyst the composition of which includes Cr_2O_3 (14.5 mass%–15.5 mass%), K_2O (2 mass%–2.5 mass%), and lanthanides (4.5 mass%–5 mass%).[35]

The principal disadvantage of the synthesis of 2-methylthiophene from piperylene and hydrogen sulfide is the comparatively short operating lifetime of chromium-containing catalysts. For example, the catalysts (compositions in mass%) 18 Cr_2O_3 – 4 K_2O – 78 Al_2O_3 (Cr, K, Al) and 5 Cr_2O_3 – 1 K_2O – 5 La_2O_3 – 89 Al_2O_3 (Cr, K, La, Al) have a high initial activity: the yields of 2-methylthiophene in their presence are respectively 60 mass% and 40 mass% relative to the piperylene passed through the system.[36] However, after they have been used for only 3–4 h, their activity begins to fall and after 6–7 h the yields diminish to 12 mass% and 22 mass% respectively. The less marked decrease in the activity of the Cr, K, La, Al catalyst is apparently associated with the presence of lanthanum oxide in

the latter. The experiments were performed at 500 °C, v_{sp} = 0.3 to 0.5 h^{-1}, and $H_2S:C_5$ = (2–4):1. These catalysts have a running-in period of 1.5–2 h. Their activity is fully restored after regeneration with an air–nitrogen mixture containing 10 vol.%–11 vol.% of oxygen at 550–580 °C for 5–7 h. After 8–10 regeneration cycles, the activity of the catalyst diminishes somewhat and then stabilises. Preliminary treatment of the catalyst with hydrogen makes it possible to increase its operating lifetime to 150 cycles at a constant activity and to increase the yield of 2-methylthiophene by a factor of 1.5–2 (35%–50%).[36]

The formation of thiophenes from diene hydrocarbons (butadiene, isoprene, and piperylene) and hydrogen sulfide has been investigated in the presence of the sulfided oxides and sulfides of metals in Periods 3–6 in the absence of a carrier. The experiments were performed at 200–550 °C, for a contact time of 1.2–6 s, and for a 1:1 molar ratio of the diene and hydrogen sulfide in the presence of sulfided Fe, V, Mo, Co, Cr, Mn, Ni, Cu, Ti, Zr, Mg, Si, and Al oxides as well as Re, Pd, Pt, and W sulfides. Catalysts containing reactive sulfur weakly bound to the catalyst surface were the most active. It has been suggested that thiophenes are formed by a multistage mechanism. This is confirmed by the fact that thiophene can be obtained both from a diene–hydrogen mixture and when only the diene is passed over the sulfided catalyst surface. In the latter case, thiophene cannot be formed without the participation of the sulfur in the catalyst. The rates of interaction of the diene with the catalyst sulfur and of the synthesis of thiophene from the diene–hydrogen sulfide mixture are similar. Consequently hydrogen sulfide does not participate directly in the formation of thiophene and is required to maintain a stationary state of the sulfide catalyst surface. The yields of 2- and 3-methylthiophenes from piperylene and isoprene were respectively 55.0 mol% and 45.0 mol% (relative to the C_5 hydrocarbon passed through the system) in the presence of sulfided vanadium oxide at 420 °C and for a contact time of 3 s. The activity of the catalyst was estimated from the specific rate of formation of thiophenes, which was calculated in accordance with a first order equation and was referred to the unit catalyst surface. The most active catalysts are Re, V, Fe, Mo, and platinum metal sulfides. The activation energies for the formation of thiophenes from various dienes are similar.[37,38]

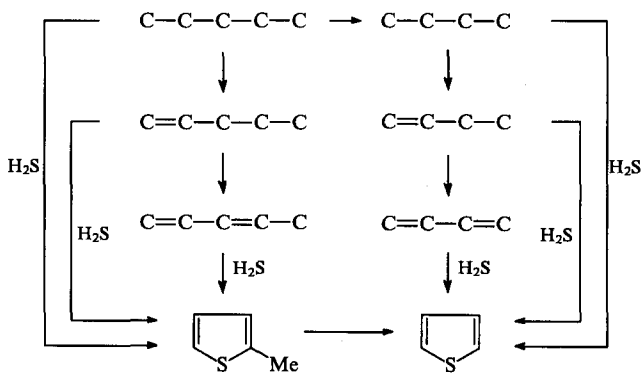
In order to estimate the activity of C_5 hydrocarbons of different structure in heterocyclisation processes, the interaction of n-pentane, pent-1-yne, isopentane, 2-methylbut-2-ene, and isopentenes with hydrogen sulfide in the presence of a Cr, K, Ln, Al catalyst was investigated.[39–42] The comparison was carried out at 550 °C, v_{sp} = 0.3–0.9 h^{-1}, and $H_2S:C_5$ = 2. The presence of CO_2 and N_2 in the reaction medium influences the selectivity of the catalyst. Under a CO_2 atmosphere, the yield of the heterocyclisation products increases and the cracking function of the catalyst is weakened. Under these conditions, the yield of liquid products increases from 60% to 98%. In terms of their capacity to undergo heterocyclisation in the presence of the Cr, K, Ln, Al catalyst, C_5 hydrocarbons can be arranged in the sequence n-pentane < pent-1-yne < isopentenes < isopentane < 2-methylbut-2-ene. Hydrocarbons with the iso-structure exhibit a higher reactivity in the formation of methylthiophenes than hydrocarbons with the normal structure. The yield of 2-methylthiophene from n-pentane and hydrogen sulfide is 55.3%, while the yields of 3-methylthiophene from isopentane and 2-methylbut-2-ene are 74.9 mass% and 79.5 mass% (relative to the hydrocarbon passed through the system) respectively. The heterocyclising properties of rhenium oxides and sulfides deposited on aluminium oxide are manifested in the interaction of n-pentane with hydrogen sulfide.[41–43] The yield of 2-methylthiophene at 550 °C, v_{sp} = 0.8–0.9 h^{-1}, and H_2S: n-C_5 = 2 in the presence of 5% of rhenium in the catalyst did not exceed 8%.

Under the same conditions, thiophene and 3-methylthiophene are formed respectively in yields of 19.2% and 12.1% (relative to the n-pentane passed through the system) together with 18.8% of 2-methylthiophene in the presence of the catalyst (composition in mass%) 2 Re_2O_7–2 Cr_2O_3–5 Ln–81 Al_2O_3. The catalytic reaction mixture contains also up to 10% of CS_2. Carbon dioxide and nitrogen have different effects on the selectivity of the reaction. In nitrogen, 2–3 times more of methylthiophene is formed than under a CO_2 atmosphere. 3-Methylthiophene can be produced as a result of the interaction of carbon disulfide with isopentane, which is obtained as a result of the isomerisation of n-pentane.[41]

V. The mechanism of the formation of thiophenes from C_4–C_5 hydrocarbons and hydrogen sulfide

The mechanism of the formation of 2-methylthiophene and thiophene in the presence of the Cr, La, K, Al catalyst has been investigated by the isotope-kinetic method using ^{14}C-labelled molecules.[44,45] Measurement of the concentration and of the molar radioactivity of the reaction products when n-pentane is supplied together with a small amount of added n-pentane labelled with ^{14}C makes it possible to determine the rates of individual stages of the reaction in which both pentane and pentene participate. As a rule, these rates are calculated from the dependence of the molar radioactivity on the contact time. The proposed mechanism is presented in Scheme 2.

Scheme 2



2-Methylthiophene is mainly formed consecutively from hydrogen sulfide and n-pentane via dehydrogenation products—pentenes and pentadiene. Thiophene is also formed via the hydrogenation products—butene and butadiene, with subsequent ring closure at the sulfur atom. Butane is obtained by the cleavage of a C–C bond in n-pentane. A small proportion of 2-methylthiophene is a product of the interaction of n-pentane and pentene with hydrogen sulfide, while thiophene is also partly formed by the reaction of hydrogen sulfide with n-butane or butene and by the demethylation of 2-methylthiophene.

VI. Interaction of C_6–C_8 hydrocarbons with hydrogen sulfide

In the interaction of C_6 hydrocarbons with hydrogen sulfide in the presence of chromium oxide catalysts, the heterocyclisation is accompanied by the dehydrocyclisation reaction with formation of benzene.[46] The dehydrocyclisation of n-hexane to benzene in the presence of chromium oxide catalysts has been investigated very widely. The reaction proceeds via the intermediate formation of hexenes, hexadienes, and trienes.[47] However, one cannot rule out the possibility that the dehydrocyclisation is suppressed by the hydrogen sulfide present in the system. Thus the interaction of 2,3-dimethylbuta-1,3-diene with hydrogen sulfide in the presence of the Cr, K, Al catalyst leads to the formation of only 3,4-dimethylthiophene, while dehydrocyclisation hardly occurs.[34] At 500 °C, v_{mass} = 0.2–0.3 h^{-1} and $H_2S:C_6$ = 2–1 for a reaction time of 1.25 h, the yield of 3,4-dimethylthiophene is 56%–60%.[48] The interaction of n-hexane, 2-methylpentane, hex-1-ene, hex-2-ene, hex-1-yne,

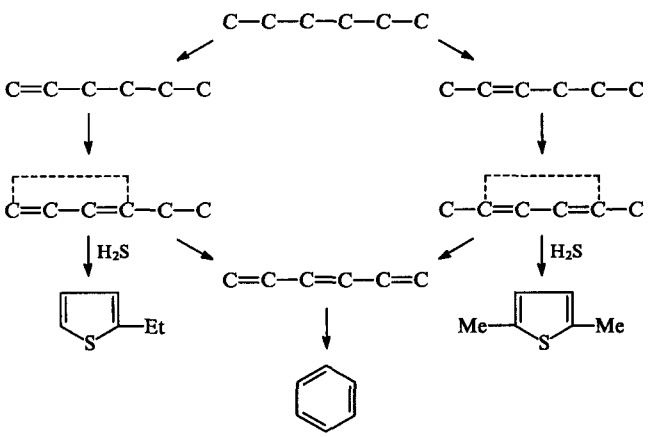
2-methylpent-1-ene, 2-methylpent-2-ene, 4-methylpent-1-ene, 4-methylpent-2-ene, and 2,3-dimethyl butane with hydrogen sulfide has been investigated in the presence of a Cr, Ln, K, Al catalyst under comparable conditions (550 °C, v_{mass} = 0.8 h^{-1}, and $H_2S:C_6$ = 4:1).[43,46] The heterocyclisation of normal C_6 hydrocarbons proceeds with formation of 2-ethylthiophene and 2,5-dimethylthiophene. In terms of their reactivity, C_6 alkanes, alkenes, and alkynes can be rearranged in the following sequence:

$$C-C-C-C-C-C \leqslant C-C=C-C-C-C$$
$$\simeq C=C-C-C-C-C < C\equiv C-C-C-C-C\ .$$

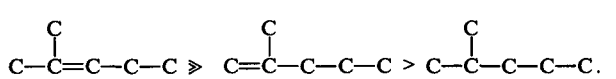
Alkynes show the highest reactivity in the heterocyclisation reaction and are followed by alkenes and alkanes. With increase in the reactivity of the hydrocarbon, the fraction of 2,5-dimethylthiophene in the reaction products increases compared with 2-ethylthiophene, i.e. ring closure at the sulfur atom involves the 2–5 carbon atoms to a greater extent than the 1–4 carbon atoms. It is noteworthy that, on raising the reaction temperature to 475 °C, n-hexane undergoes dehydrocyclisation with formation of benzene, together with heterocyclisation.

On the basis of data concerning the mechanism of the formation of 2-methylthiophene from hydrogen sulfide and n-pentane, according to which the reaction proceeds via alkenes and alkadienes,[44,45] one can postulate that 2,5-dimethylthiophene and 2-ethylthiophene are formed by a similar mechanism (Scheme 3).

Scheme 3



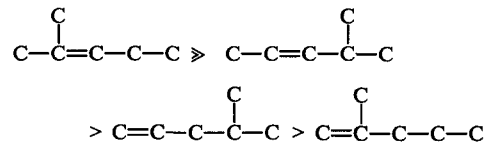
In the synthesis of dialkylthiophenes by the reaction of C_6 hydrocarbons having the iso-structure with hydrogen sulfide, there is virtually no dehydrocyclisation. In terms of their tendency to undergo heterocyclisation, the C_6 iso-hydrocarbons investigated can be arranged in the sequence



The yields of 2,4-dimethylthiophene from the above compounds are 40.2%, 23.4%, and 11.8% respectively (relative to the hydrocarbon passed through the system).

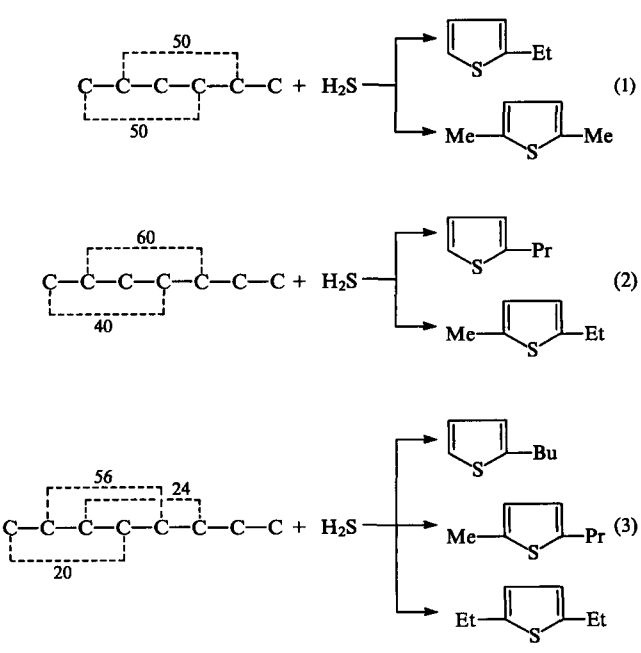
The position of the methyl group in α-alkenes hardly affects the yield of 2,4-dimethylthiophene and influences only the yield of 2-methylthiophene. The latter is a product of the interaction of hydrogen sulfide with pentane, which is formed owing to the dissociation of a C–C bond in the alkene. Thus the yield of 2-methylthiophene in the interaction of hydrogen sulfide with 4-methylpent-1-ene is twice as great as in the interaction with 2-methylpent-1-ene. The presence of a methyl group in β-alkenes promotes heterocyclisation. The yield of 2,4-dimethylthiophene is 40.2% from 2-methyl-pent-2-ene and 26.4% from 4-methylpent-2-ene.[43,46]

Thus, C_6 α- and β-isoalkenes with a methyl group in different positions in the hydrocarbon chain can be arranged in the following sequence in terms of their tendency to undergo the heterocyclisation reaction (the yields of 2,4-dimethylthiophene are 40.2%, 26.4%, 23.4%, and 22.4% respectively):



Thermodynamic analysis showed that experimental yields of the products of the heterocyclisation and dehydrocyclisation of n-hexane at 820 K are 82.8% (alkylthiophenes) and 81% (benzene), while at 750 K the corresponding yields are 24.4% and 10% respectively relative to the equilibrium yields.[49] In the interaction of C_6 normal alkenes and isoalkenes with hydrogen sulfide at 820 K, the heterocyclisation reaction virtually reaches equilibrium and the yields of ethyl- and dimethylthiophenes are 81.7%–97.8% of the equilibrium values (taking into account side reactions). The reactivity of n-alkanes, which give rise to alkylthiophenes and aromatic hydrocarbons on interaction with hydrogen sulfide, depends on their chain length.[50] In the presence of a Cr, Ln, K, Al catalyst at 450 °C, v_{mass} = 0.8 h^{-1}, and H_2S : n-C_6(n-C_7, n-C_8) = 2 under a nitrogen atmosphere, mainly 2-ethylthiophene and 2,5-dimethylthiophene are obtained from n-hexane, 2-propylthiophene and 2-methyl-5-propylthiophene are obtained from n-heptane and 2-butylthiophene, 2,5-diethylthiophene, and 2-methyl-5-propylthiophene are obtained from n-octane [reactions (1)–(3), Scheme 4]. Dehydrocyclisation results in the formation of benzene and toluene respectively from normal hexane and heptane, while ethylbenzene and *o*-xylene are formed from n-octane. The numerals in Eqns (1)–(3) (Scheme 4) represent the percentage contributions of the ring closure reactions at the sulfur atom involving the 1–4, 2–5, and 3–6 carbon atoms. Heterocyclisation with formation of the thiophene ring, proceeds as shown in relation to n-hexane, with ring closure at the sulfur atom involving the carbon atoms in the 1- and 4-positions or the 2- and 5-positions. With increase in the chain length of the alkane from C_6 to C_7, the fraction of alkylthiophenes formed via ring closure at the sulfur atom involving the carbon atoms in the 2- and 5-positions increases. In the case of n-octane, the 1–4 and 2–5 heterocyclisations are accompanied also by ring closure at the sulfur atom involving the carbon atoms in the 3- and

Scheme 4



6-positions. With increase in the chain length of the n-alkane, the yield of the heterocyclisation product diminishes, while the yield of the dehydrocyclisation product increases. The molar ratios of alkylthiophenes and aromatic hydrocarbons formed in the interaction of hydrogen sulfide with n-hexane, n-heptane, and n-octane are respectively 5.5, 1.25, and 0.7.

As shown for the interaction of hydrogen sulfide with n-hexane, the alkylthiophene and benzene formation reactions probably include a common stage involving the dehydrogenation of alkanes to unsaturated hydrocarbons. The longer the n-alkane chain, the more readily the unsaturated hydrocarbons obtained undergo closure to an aromatic ring compared with ring closure at the sulfur atom with formation of the thiophene ring.[50] The different abilities of n-alkanes (depending on the chain length) to enter into heterocyclisation or dehydrocyclisation reactions in the presence of chromium oxide catalysts may have to be taken into account in considering the genesis of petroleum containing both aromatic and thiophene oxide compounds.

VII. Physicochemical properties of chromium-containing oxide catalysts

The active chromium-containing heterocyclisation catalysts have been investigated by various physicochemical methods.[51–53] X-Ray diffraction analysis of the Cr, La, K, Al catalyst after the heterocyclisation reaction has been carried out in its presence (560 °C, v_{mass} = 225 h^{-1}, $H_2S:C_n$ = 2.0, yield of thiophene 33.2% after 3 h) demonstrated the presence of the crystalline γ-Al_2O_3 phase. The addition of potassium and lanthanum oxides does not affect the phase composition of the aluminium oxide–chromium oxide catalyst.[51] The formation during the heterocyclisation process of a solid solution of Cr_2O_3 in Al_2O_3, accompanied by an increase in the unit cell parameter from 7.90 to 7.95 Å, is influenced by the Cr_2O_3 content and the reaction conditions.

In order to account for the effect of added potassium and lanthanum oxides on the heterocyclising properties of the aluminium oxide–chromium oxide catalyst, the optical and EPR spectra of the oxidised and reduced specimens were analysed.[53–55] The catalysts were reduced at a pressure of 200–300 Torr and a temperature of 580 °C for 1 h. The optical and EPR spectra were obtained for the same specimens. After the catalysts had been treated at 500–700 °C in air or under a helium atmosphere, Cr^{6+}, Cr^{5+}, and Cr^{3+} ions were detected in them. The optical spectra of the reduced catalyst contain three absorption maxima: at 22 300, 16 200, and 10 200 cm^{-1}. The absorption maxima at 22 300 and 16 200 cm^{-1} are typical for aluminium oxide–chromium oxide catalysts. Octahedrally coordinated Cr^{3+} ions are responsible for them. The 10 200 cm^{-1} maximum is due to square-pyramidal Cr^{3+} ions. This maximum vanishes after the adsorption of water and hydrogen sulfide molecules. Hence it follows that these ions are in fact the centres for the adsorption of H_2O and H_2S. The adsorbed molecules enter the first coordination spheres of the above ions, increasing their coordination to octahedral.

It follows from analysis of the optical spectra of the reduced specimens that the nature of the spectra is independent of the lanthanum and potassium oxides added to the aluminium oxide–chromium oxide catalyst. On the other hand, the EPR spectra of the reduced catalysts do depend on these additives. They contain in all cases a broad asymmetric band, which results from superposition of signals due to the magnetically concentrated phase (β-phase) and the magnetically dilute phase (δ-phase) of the Cr^{3+} ions. In the spectra of the specimens containing added lanthanum and potassium oxides, the width of the band due to the β-phase (ΔH = 900 Oe) is much smaller than in the spectrum of the aluminium oxide–chromium oxide catalyst (ΔH = 1150 Oe). The additives influence the state of the Cr^{3+} ions in the catalyst.

Preliminary heat treatment of the specimens at 700 °C (the last stage of the preparation of the catalyst) increases the amount of chromium ions responsible for the appearance of the absorption maximum at 10 200 cm^{-1}, i.e. the surface square-pyramidal coordinated Cr^{3+} ions.

The above spectroscopic data for the Cr, La, K, Al catalysts agree with the results obtained for the aluminium oxide–chromium oxide catalyst for the dehydrogenation of alkanes.[53–55] The Cr, Ln, K, Al catalyst is active both in the heterocyclisation of hexane in the reaction with hydrogen sulfide and in the dehydrocyclisation of n-hexane to benzene. Both reactions proceed via common stages involving the dehydrogenation of alkanes to alkenes and alkadienes.[46]

The content of the lowest-valence chromium and lanthanide ions in the above catalyst was determined from the chemisorption of oxygen at 20 °C.[56] The Cr^{2+} ions are formed in the aluminium oxide–chromium oxide catalyst only on reduction above 300 °C, while at 500 °C their amount reaches a maximum.[57] The compositions of the dehydrogenating centres of the aluminium oxide–chromium oxide dehydrogenation and dehydrocyclisation catalysts include Cr^{2+} ions.[58] After the reduced catalysts have come into contact with O_2 at 20 °C, oxygen is first chemisorbed on the Cr^{2+} ions, but there is also a possibility of its chemisorption on the coordinatively unsaturated Cr^{3+} ions. In a reducing medium, under the conditions of the synthesis of 2-methylthiophene at 550 °C, the aluminium oxide–chromium oxide catalyst, without additives and with added potassium and lanthanum oxides, contains Cr^{2+} ions on which the dehydrogenation stages, common to heterocyclisation and dehydrocyclisation, most probably occur. Indeed, we find that (a) in the absence of Cr^{2+} ions the above reactions do not occur on the catalyst, (b) the number of active dehydrogenation centres, found from the curves for the poisoning of the catalyst with oxygen during the dehydrogenation of isopentane, agrees with the number of Cr^{2+} ions determined by titration with iron ammonium alum, and (c) the dehydrogenating and dehydrocyclising activities of the aluminium oxide–chromium oxide, aluminium oxide–chromium oxide–potassium oxide, and aluminium oxide–chromium oxide–calcium oxide catalysts increase in proportion to their Cr^{2+} content.

As in the dehydrocyclisation catalysts, in the heterocyclisation catalysts potassium oxide influences the productivity of the active centres because it alters the environment of the Cr^{2+} ion and its energetic characteristics. The lanthanum oxides in the aluminium oxide–chromium oxide catalyst also play the role of a promoting agent and not of the main active dehydrogenation component, although their amount is the same (5 mass%) as that of chromium oxide. Lanthanide ions in a low-valence state, with very powerful electron-donating properties and capable of functioning as dehydrogenation active centres, have been detected in the Cr, Ln, K, Al catalyst.[56]

It has been shown by X-ray photoelectron spectroscopy that the surface concentration of chromium on the 5% Cr_2O_3–95% Al_2O_3 catalyst decreases by a factor of two after the heterocyclisation reaction, whereas no change in the chromium concentration was observed after the addition of potassium and lanthanide oxides.[43] During the reaction, Cr^{6+} and Cr^{5+} are reduced mainly to Cr^{3+}.

It follows from the data obtained that the aluminium oxide–chromium oxide heterocyclisation catalysts promoted by potassium and lanthanide oxides contain low-valence chromium and lanthanide cations, which may form part of the composition of the catalyst active centres.[56] A study of the properties of the chromium ions in different oxidation states on the surfaces of chromium-containing catalysts by optical and EPR spectroscopy has been described in a review.[59]

Table 3. Catalytic synthesis of thiophenes by the reaction of C_2 and C_4-C_6 hydrocarbons with hydrogen sulfide in the presence of oxide catalysts.

Hydrocarbon	Catalyst composition (mass%)	T/°C	v_{sp}/h^{-1}	$H_2S:C_n$	Yield relative to hydrocarbon passed through system (mass%)	Thiophenes	Ref.
Acetylene	Al_2O_3	425–450	392[a]	1.5	38.4	Thiophene	7
Acetylene, electrocracking gas (29 vol.% C_2H_2, 57 vol.% H_2)	Al_2O_3	540–560	392[a]	1.5	50.2	"	7, 8
Butane	5 Cr_2O_3, 5 La_2O_3, 90 Al_2O_3	580	1.2–1.3	2–2.2	38–40	"	15
	5 Cr_2O_3, 5 La_2O_3, 1 K_2O, 89 Al_2O_3	580	1–1.2	2–2.5	40.0	"	16
Butene	5 SiO_2, 10 MoO_3, 85 Al_2O_3	590	1.7	1.6	52.9	"	14
But-2-ene	5 SiO_2, 10 MoO_3, 85 Al_2O_3[b]	590	1.7	1.5	55.4	"	14
	5 SiO_2, 10 Cr_2O_3, 85 Al_2O_3	590	1.4	2–2.4	53.3	"	14
	5 Cr_2O_3, 5 La_2O_3, 1 K_2O, 85 Al_2O_3	580	0.9	2.1	52.0	"	16–18
Buta-1,3-diene	5 Cr_2O_3, 1 K_2O, 94 Al_2O_3	500	1.0	2.1	49.0	"	16–18
	5 Cr_2O_3, 5 La_2O_3, 1 K_2O, 89 Al_2O_3	500	1.0	4.2	51.0	"	16–18
		580	0.9–1.2	2.1–2.6	55.0	"	16–18
Butane–butene fraction	5 Cr_2O_3, 5 BBF,[c] 1 K_2O, 89 Al_2O_3	580	130–140[a]	2.2	90.9		22–24
Pentane	5 Cr_2O_3, 5 BBF,[c] 1 K_2O, 89 Al_2O_3	550	0.3–0.4	2.0	45	Methylthiophene	39, 41
Pent-1-ene	15 SiO_2, 10 MoO_3, 85 Al_2O_3	570	1.6	1.8	33.3	"	14
Pent-1-yne	15 Cr_2O_3, 5 BBF,[c] 1 K_2O, 89 Al_2O_3	550	0.5	2.0	68.3	"	39, 41
Piperylene	18 Cr_2O_3, 4 K_2O, 78 Al_2O_3	500	0.3	2.6	69.9	"	31, 34
	5 Cr_2O_3, 5 BBF,[c] 1 K_2O, 89 Al_2O_3	500	0.3	2.0 (N_2)	71.4	"	41

Isopentane	5 SiO_2, 10 MoO_3, 85 Al_2O_3	530	1.6	1.9	22.8	3-Methylthiophene	14
2-Methylbutane	12 Cr_2O_3, 5 K_2O, 83 Al_2O_3	500	0.32	2.0 (N_2)	70.1	"	20
2-Methylbut-2-ene	5 Cr_2O_3, BBF[c] 1 K_2O, 89 Al_2O_3	550	0.3	2.0	79.5	"	41
	12 Cr_2O_3, 5 K_2O, 83 Al_2O_3	500	0.22	22.0 (N_2)	84.7	"	20
	12 Cr_2O_3, 5 Li_2O, 83 Al_2O_3	500	0.17	2.0 (N_2)	58.8	"	20
	12 Cr_2O_3, 5 Na_2O, 83 Al_2O_3	500	0.22	2.0 (N_2)	63.2	"	20
	12 Cr_2O_3, 5 MgO, 83 Al_2O_3	500	0.17	2.0 (N_2)	43.0	"	20
	12 Cr_2O_3, 5 CaO, 83 Al_2O_3	500	0.18	2.0 (N_2)	51.4	"	20
	18 V_2O_5, 2 ThO_2, 2 K_2O,78 Al_2O_3	410	0.4	2.0	56.6	"	21
3-Methylbut-1-ene	12 Cr_2O_3, 5 K_2O, 83 Al_2O_3	500	0.22	2.0 (N_2)	81.2	"	20
Isopentenes	5 Cr_2O_3, 5 BBF,[c] 1 K_2O, 89 Al_2O_3	550	0.5	2.0	61.6	"	46
2-Methylpent-2-ene	5 Cr_2O_3, 5 BBF,[c] 1 K_2O, 89 Al_2O_3	550	0.8	4.0	40.2	2,3-Dimethylthiophene	46
2,3-Dimethylbutane	5 Cr_2O_3, 5 BBF,[c] 1 K_2O, 89 Al_2O_3	480	0.4	5.0	56.9	3,4-Dimethylthiophene	46
2,3-Dimethylbutadiene	18 Cr_2O_3, 4 K_2O, 78 Al_2O_3	500	0.2	2.0	60.0	"	48

[a] The ratio of the volume of gaseous hydrocarbons to the volume of the catalyst in 1 h; in the remaining cases—the ratio of the volume of liquid hydrocarbons to the volume of the catalyst.
[b] In a fluidised catalyst bed.
[c] Composition of lanthanide oxides (%): 2.7 CeO_2, 1.3 La_2O_3, 0.75 Nd_2O_3, 0.25 Pr_2O_3.

VIII. Industrial methods of synthesis of thiophenes

The Pennwalt Corporation in the USA and the Croda Synthetic Chemicals, Ltd and Pennwalts Holland B.V in Europe are known to produce various thiophenes.[60] The requirement by the world market for thiophene in 1982 amounted to 1000–1400 tonnes.

The synthesis is based on the interaction of butene and butadiene with carbon disulfide (as a source of sulfur) in contact with methane or CO_2 at 500 °C in the presence of an 11% chromium oxide catalyst promoted by alkali metals (6% K_2CO_3). The catalyst is regenerated periodically to remove the coke deposit. This process can also be used to obtain 2- and 3-alkyl-thiophenes from C_6 hydrocarbons.[61]

A plant in which thiophene was produced from C_4 hydrocarbons and fused sulfur — the Socony-Vacuum process — began operating in the USA in the 1950s.[6] The process is carried out at temperatures up to 700 °C and atmospheric pressure. Apart from the high temperature, a disadvantage of this procedure is appreciable tar formation, etc.

Thiophene is obtained also from a mixture of butane, gaseous sulfur, and hydrogen sulfide in the presence of 19% Cr_2O_3–81% Al_2O_3 catalyst at 500 °C (yield: 49% after 168 h). The maximum conversion into thiophene is attained for a ratio H_2S : n-C_4H_{10} = 15 : 1. The temperature in the reactor is maintained by the reaction between sulfur and side products. The hydrogen evolved on dehydrogenation of n-butane reacts with sulfur to form hydrogen sulfide; this highly exothermic reaction compensates for lack of external heating. Corrosion of the reactor is thereby greatly reduced. The catalyst is regenerated periodically. The method makes it possible to increase the yield of thiophene compared with the Socony-Vacuum process, to reduce corrosion, and to diminish tar formation. By this procedure, one can obtain 2- and 3-methylthiophenes from the corresponding hydrocarbons.

There is a possibility of synthesising thiophenes from the gases generated in the semicoking of shale.[63] Apart from C_1–C_5 hydrocarbons, the semicoking gases contain also CO, CO_2, and hydrogen sulfide, the content of which can reach 5%–12%. At 650 °C in the presence of the hydrogen sulfide-treated Cr, La, K, Al catalyst, the yield of the liquid catalytic reaction mixture containing 71.3% of thiophene is 85%. This method of synthesis may prove promising in countries possessing deposits of shale raw material containing sulfur compounds.

* * *

One of the main tasks in modern petroleum processing is rational use of the hydrocarbon raw material and hydrogen sulfide. The employment of oxide catalysts makes it possible to obtain thiophene and alkylthiophenes by the heterocyclisation of C_2 and C_4–C_8 hydrocarbons with participation of hydrogen sulfide. Table 3 indicates the optimum conditions and compositions of the active heterocyclisation catalysts. The reaction of hydrogen sulfide with the acetylene-containing gas generated in electrocracking on γ-Al_2O_3 may be of practical interest. Thiophenes can be obtained in appreciable yields by the reaction of C_4–C_6 hydrocarbons with hydrogen sulfide in the presence of chromium-containing oxide catalysts. In order to increase the yield of thiophenes, it is useful to employ the butane–butene fraction and hydrogen sulfide and to carry out the reaction in a vibrofluidised bed. 2-Methylthiophene may be obtained (in a yield up to 68%) from hydrogen sulfide and piperylene, while 3-methylthiophene may be obtained (in 75% yield) from hydrogen sulfide and isopentane. The results obtained in the study of the interaction of hydrogen sulfide with C_6 hydrocarbons having the iso-structure also merit attention: 3,4- and 2,4-dimethylthiophenes have been synthesised in this way from 2,3-dimethylbutane and 2-methylpent-2-ene respectively. Thus processes involving the catalytic synthesis of thiophenes from a petrochemical raw material — hydrocarbons and hydrogen sulfide — can be used successfully to satisfy the increasing need for these heterocycles.

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