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Heterogeneous catalytic synthesis of alkanethiols and dialkyl sulfides from alcohols and hydrogen sulfide

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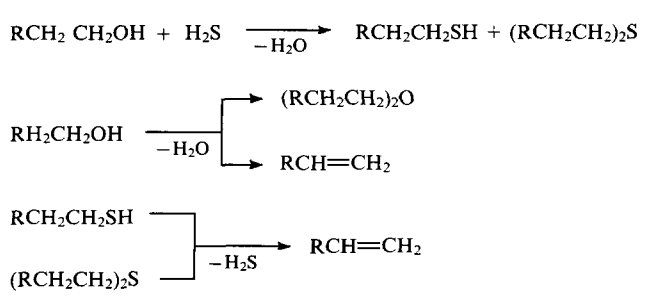
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Abstract. The results of studies of the heterogeneous acid-base catalysis of reactions of alcohols with hydrogen sulfides, which yield alkanethiols and dialkyl sulfides, are surveyed. Data concerning the activity and selectivity of the catalysts under the reaction conditions are considered. A relation is established between the catalytic and acid – base properties of the catalysts. The mechanism of the thiolation reaction is discussed and the criteria for the selection of the effective catalysts are formulated. The bibliography includes 97 references.

I. Introduction

Catalysis has played an important role in the development of the chemistry of organic compounds of sulfur.[1] This applies also to the synthesis of compounds with thiyl and sulfide groups, in particular of alkanethiols and dialkyl sulfides, which have valuable properties and have therefore found extensive applications.

Alkanethiols and dialkyl sulfides may be obtained also by noncatalytic methods, but these require the employment of expensive starting materials, which are in many cases difficult to obtain. It is more convenient to synthesise these substances from the industrially produced alcohols and hydrogen sulfides.



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The thermodynamic feasibility of reactions involving the formation of alkanethiols and dialkyl sulfides from alcohols and hydrogen sulfide, the dehydration of alcohols with formation of a dialkyl ether and an alkene, and the decomposition of alkanethiols and dialkyl sulfides with formation of hydrogen sulfides and alkenes is very high.[1–5]

The conversion of alcohols into thiols occurs only in the presence of catalysts. By regulating their composition and the reaction conditions, it is possible to direct the process towards the formation of the desired product. The heterogeneous-catalytic method of synthesis of alkanethiols and dialkyl sulfides is the most promising because it is highly productive and is susceptible to technological application, which makes it possible to simplify the isolation of the reaction products and the catalyst from the reaction medium and to reduce the amount of ecologically harmful waste.

The practical application of effective processes leading to the synthesis of alkanethiols and dialkyl sulfides requires active and selective solid catalysts. In 1910, Sabatier[6] was the first to use a solid catalyst (thorium dioxide) in the gas-phase reactions of alcohols with hydrogen sulfide, which lead to the formation of alkanethiols and dialkyl sulfides. In 1921, this reaction was achieved[7] in the presence of ThO_2 deposited in an amount of 25 mass% on pumice, at 260 – 380 °C, atmospheric pressure, and for the molar ratio H_2S : alcohol = 0.75 – 2.0. The main products of the reactions of hydrogen sulfide with methanol, ethanol, 1- and 2-butanols, and 2-pentanol were the corresponding thiols, with yields of 35% – 52%; aldehydes were also formed in yields up to 20% together with small amounts of alkenes and traces of dialkyl sulfides. During the first world war, this catalyst was used to produce butane-1-thiol from 1-butanol and hydrogen sulfide.[2,8,9] Further studies were directed to the search for more active and selective catalysts, which led to the creation abroad in the 1950s – 1970s of industrial processes in which unpromoted alumina was employed initially and then also other catalysts. However, neither the technology of the manufacturing process nor the catalysts employed are known.[8]

The available information about the catalysts and the conditions in the synthesis of alkanethiols and dialkyl sulfides from alcohols and hydrogen sulfide referring to the period up to 1970 – 1975 is contained mainly in patents and the reviews based on them.[2,8–10] It is claimed that catalysts active in the syntheses of methanethiol and dimethyl sulfide may be used in the synthesis of alkanethiols and dialkyl sulfides from hydrogen sulfide and various alcohols, but specific examples almost always refer to the reaction of methanol with hydrogen sulfide. Certain theoretical publications also appeared during this period, but the relevant

studies were not systematic and no attempts were made at a quantitative comparison of the properties of the catalysts in the thiol formation processes. Since the publication of the reviews mentioned above,[2,8-10] data have accumulated, but have not yet been arranged systematically, on the catalysts used in the gas-phase heterogeneous synthesis of alkanethiols and dialkyl sulfides from alcohols and hydrogen sulfide and on the mechanism of the thiolation reactions, which is important for the prediction of the catalytic action and the creation of new effective catalysts. These data are surveyed in the present review.

II. Catalysts for the conversion of alcohols into thiols by hydrogen sulfide

Alcohols are converted into thiols by treatment with hydrogen sulfide in the presence of both massive and supported catalysts. The rate of reaction (w) and the selectivity (S) in the formation of the thiol and the sulfide, which is equal to the ratio of the yield of the corresponding product to the degree of conversion of the alcohol (x), depend on the reaction conditions: temperature, molar ratio of hydrogen sulfide to the alcohol (M), the pressure (P)†, and the contact time (τ)‡.

1. Metal oxides and sulfides

The reaction of alcohols with hydrogen sulfides is accelerated, albeit to different extents, by massive metal oxides and sulfides. Silicon dioxide is relatively ineffective in the conversion of alcohols into thiols.[11-13] Thus, in the interaction of methanol with hydrogen sulfide in the presence of SiO_2, the yields of methanethiol and dimethyl sulfide were 5 mol% and 1.2 mol% respectively (360 °C, M = 0.6–1.6, τ = 42 s, $x \leqslant 20\%$).[11,12] The activity of magnesium oxide is also low in this reaction: the yield of methanethiol was 2 mol%–3 mol% (350 °C, M = 0.5–2.0, $\tau \approx 2$ s).[14] The reaction of 1-butanol with hydrogen sulfide on MgO leads to the formation of butane-1-thiol and butene in 32 mol% and 50 mol% yields respectively (300 °C, M = 10, τ = 21 s, x = 62%).[15] High yields of sulfur-containing products have been attained in the conversion of alcohols into thiols on a series of massive oxides. It has been found[14] that, in the interaction of methanol with hydrogen sulfide on TiO_2 (anatase), the selectivity with respect to methanethiol is 31% and 57% and that with respect to dimethyl sulfide is 52% and 41% respectively for M = 0.5 and 2.0 (350 °C, $\tau \approx 5$ s, and x = 32%–91%). On TiO_2 (rutile), the degree of conversion under these conditions is lower (15%–45%), but a high selectivity with respect to methanethiol and a reduced selectivity with respect to dimethyl sulfide are observed (85%–95% and 3% respectively). Methanol decomposes with formation of methane on both modifications of TiO_2. The conversion of ethanol into the thiol takes place less selectively on TiO_2: dimethyl ether (15%) and ethene (19%) are formed in addition to ethanethiol and diethyl sulfide [yields 56 mol% and 9 mol% respectively (320 °C, M = 2.5, x = 97%)].[2] Tungsten and vanadium oxides exhibit a high activity in the conversion of alcohols into thiols. Thus, on WO_3 at 360 °C and for M = 1.6, the yield of methanethiol corresponding to the complete conversion of methanol was 81 mol% (τ = 0.5 s), whilst the yield of dimethyl sulfide was 31 mol% (τ = 4.2 s).[11]

The activities of the Mg, Ti, Zr, Ce, and Al oxides in the reaction of methanol with hydrogen sulfide for M = 0.5–2.0, 350 °C, and τ = 2–6 s have been compared.[14] It was found that the degree of conversion of the alcohol diminishes on all the catalysts with decrease in the H_2S:CH_3OH molar ratio and the selectivity with respect to methanethiol falls, but the selectivity with respect to dimethyl sulfide increases. The oxides investigated differ in their catalytic properties. Thus the activities of the oxides in the conversion of methanol into the thiol (for M = 1) vary in the following sequence:

$$Al_2O_3\,(99) > CeO_2\,(59) \geqslant TiO_2\ \text{(anatase)}\,(52) > > ZrO_2\,(34) > MgO\,(3)\ .$$

The degree of conversion of methanol [x(%)] is indicated in brackets. The catalysts can be arranged in approximately the same sequence in terms of the selectivity in the formation of dimethyl sulfide (the selectivity expressed in % is given in brackets):

$$Al_2O_3\,(84) > TiO_2\ \text{(anatase)}\,(57) > ZrO_2\,(9) \geqslant \geqslant CeO_2\,(7) > MgO\,(0)\ .$$

On the other hand, the virtually opposite sequence is observed for the variation of the selectivity of the catalysts with respect to methanethiol:

$$MgO\,(100) > ZrO_2\,(90) > CeO_2\,(50) > > TiO_2\ \text{(anatase)}\,(36) > Al_2O_3\,(15)\ .$$

The authors[14] attribute the observed variations to the different acid–base characteristics of the above oxides. The strong basic centres in magnesium oxide and the higher electronegative charge on the oxygen atom promote a low degree of conversion of methanol and a high selectivity with respect to methanethiol.

The low rate of the reaction of methanol with hydrogen sulfide on certain oxides can be explained also by their low specific surfaces (for example, the specific surface of ZrO_2 is 18 $m^2\ g^{-1}$ and that of ZrO is 5.4 $m^2\ g^{-1}$). Mashkina et al.[11] inferred the relative activities of the oxides from the rate of reaction per unit surface for a constant degree of conversion achieved by varying the contact time. The highest rate of conversion of methanol and a high selectivity with respect to methanethiol are observed on tungsten and vanadium oxides; aluminium and titanium oxides are approximately an order of magnitude less active, while Zr, Be, Mg, Zn, and Si oxides are less active by 2–3 orders of magnitude (Table 1). The specific activities of the majority of the oxides investigated increase with increase in the ionisation potentials of the cations (Table 1), which may indicate a dependence of the activity on the electron-accepting capacity of the cation.

Table 1. The specific activities and selectivities of metal oxides in the reaction of methanol with hydrogen sulfide (360 °C, M = 1.6, x = 50%–60%).[11]

Catalyst (ionisation potential/eV)	w/ mmol $m^{-2}\ h^{-1}$	S (%)	
		CH_3SH	$(CH_3)_2S$
SiO_2 (45.13)[a]	0.006	22	7
BeO_2 (18.21)[a]	0.04	47	0
MgO (15.03)[a]	0.05	65	0
ZrO_2 (33.97)	0.06	85	4
ZnO (17.96)	0.10	0	12
TiO_2 (43.24)	1.2	56	27
γ-Al_2O_3 (28.44)	1.9	37	35
η-Al_2O_3 (28.44)	3.2	35	38
WO_3 (56)	32	73	13
V_2O_5 (65.2)	44	85	0.4

[a] $x \leqslant 40\%$.

† In most cases, the experiments are carried out at P = 0.1 MPa, so that henceforth the pressure will be indicated only when it is higher than atmospheric.

‡ The contact time τ is equal to the ratio of the volume of the catalyst (in ml) to the gas flow rate (in ml s^{-1}) at 20 °C and P = 0.1 MPa. In certain cases the values of τ calculated from the volume flow rates quoted in the relevant communications have been used in the review; such quantities are designated by the symbol $\approx$.

Although the activity of aluminium oxide calculated per m^2 of the surface area is low, it has an advantage over other massive oxides, since it can have a large surface area thus ensuring a high activity per unit weight of catalyst. Furthermore, Al_2O_3 is fairly thermostable, is relatively readily available, and is cheap. For this reason, it was initially preferred to use Al_2O_3 as the catalyst for the conversion of alcohols into thiols.[2,8] In the interaction of methanol with hydrogen sulfide in the presence of γ-Al_2O_3, a high rate of reaction per unit weight of the catalyst is attained. The principal reaction products are methanethiol, dimethyl ether, and dimethyl sulfide, whilst under severe conditions carbon oxides and methane are also formed. In the presence of a deficit of hydrogen sulfide relative to methanol and at a high temperature, dimethyl sulfide is formed preferentially. In order to obtain methanethiol with a high selectivity, it is necessary that the hydrogen sulfide : methanol ratio should be greater than 5.[3] The phase composition of the catalyst is also improtant — γ- and η-Al_2O_3 are the most active.[11,12,16] The inadequate stability of Al_2O_3 during a prolonged thiolation reaction, caused by the saturation of the surface by coke, has been noted.[13] The high activity of aluminium oxide in the reaction involving the conversion of methanol into the thiol has been explained[11] by the presence in the oxide of paired acid–base centres promoting the activation of the reactants.

The reactions of higher alcohols with hydrogen sulfide on Al_2O_3 take place at a lower temperature than the reaction of methanol. The conversion of the alcohol into the thiol is accompanied by its dehydration with formation of an ether and an alkene, which entails a decrease in selectivity in the formation of sulfur-containing products. Table 2 presents some examples of the conversion of alcohols into thiols in the presence of Al_2O_3.

The massive Cd, Sb, Ni, W, Mo, Re, K, and Na sulfides also accelerate the interaction of alcohols with hydrogen sulfide,[2,3,11,13,20,21] although it has been noted[2] that they sometimes exhibit a reduced activity in the thiolation reaction compared with the corresponding metal oxides. Thus Sb_2S_3 has a low activity in the reaction of methanol with hydrogen sulfide: $x = 14\%$ and methanethiol is not formed, the yield of dimethyl sulfide amounting to 5 mol% (360 °C, $M = 1.6$, $\tau = 50$ s).[11] In the reaction of ethanol with hydrogen sulfide[2] on the NiW sulfide catalyst, ethanethiol is formed in 6 mol% yield (220–280 °C, $M = 3.5$, $\tau = 3.5$–4.0 s, $x = 21\%$), while on WS_2 the yield of ethanethiol is 27% (280 °C, $M = 3.3$, $\tau = 3.3$–4.0 s, $x = 99\%$). On Re_2O_7, the yield of dodecane-1-thiol, obtained from 1-dodecanol and hydrogen sulfide, is 55 mol%. The reaction is accompanied by the formation of a large amount of dodecene (240 °C, 10 MPa, duration of the experiment in an autoclave 3 h, $M = 0.7$; the reaction takes place in the presence of hydrogen).[22]

2. Aluminosilicates and zeolites

Silicon dioxide, which hardly exhibits any activity in the conversion of alcohols into thiols, acquires such an activity when some of the $(SiO_4)^{4-}$ ions are replaced by $(AlO_4)^{3-}$ ions with formation of aluminosilicates — amorphous (AlSi) and crystalline (zeolites). Thus, in the reaction of methanol with hydrogen sulfide on AlSi, the rate of conversion of methanol is 14 mmol g^{-1} h^{-1}, which is seven times higher than on SiO_2: under these conditions, the selectivity is 6% with respect to methanethiol and 62% with respect to dimethyl sulfide; dimethyl ether is formed (360 °C, $M = 1.6$, $\tau = 6.3$ s, $x = 87\%$).[11] In the presence of a reduced content of hydrogen sulfide in the reaction mixture, the selectivities with respect to methanethiol and dimethyl sulfide are 5% and 68% respectively (450 °C, $M = 0.6$, $\tau \approx 9$ s, $x = 76\%$).[23] The higher activity of AlSi compared with SiO_2 is due to the difference between their acid–base properties: SiO_2 contains only very weak proton and basic centres, while AlSi contains strong proton and Lewis acid centres as well as moderately strong basic centres, which participate in the activation of the reactants.[11] On the amorphous AlSi, 2-propanol reacts with hydrogen sulfide to form propane-2-thiol in 29%–47% yield (275–300 °C, $P = 0.9$ MPa, $M = 5$–6, $\tau \approx 0.14$–0.50 s).[19]

The conversion of alcohols into thiols is also accelerated by decationated zeolites. On HNaX, the selectivities in the formation of methanethiol and dimethyl sulfide from methanol and hydrogen sulfide are 2%–5% and 8%–19% respectively (350 °C, $M = 1$–2, $\tau \approx 6$ s, $x = 90\%$–95%),[24] whilst on HNaY (under the same conditions, for the total conversion of methanol) the selectivities are $\leqslant 10\%$ and $\leqslant 20\%$.[25,26] Best results have been obtained by employing the decationated high-silica HZSM-5 zeolite, on which the selectivity reached 5%–40% with respect to methanethiol and 50%–93% with respect to dimethyl sulfide for $\tau \approx 4.5$ s. The authors[25,26] attribute the activity of the decationated zeolites to the presence in the latter of the acid OH groups, which play the role of catalytically active centres. In the conversion of ethanol and 1-propanol into the thiols on HNaY and HZSM-5 (350 °C, $M = 1$–4, $\tau \approx 6.7$ s, $x = 70\%$–85%), the yields of the thiols did not reach 1 mol%; ethanethiol and diethyl sulfide were detected qualitatively in the ethanol conversion products, while propane-1-thiol, dipropyl sulfide, and traces of propane-2-thiol, ethanethiol, and dimethyl sulfide were detected in the 1-propanol conversion products.[27] The low selectivity is due to the dehydration of the alcohols with formation of alkenes at a high rate. In the presence of HZSM-5, 1-butanol is also only dehydrated with formation of but-1-ene and but-2-ene in the presence of a large excess ($M = 10$) of hydrogen sulfide (300 °C, $M = 10$, $\tau = 0.003$–0.025 s, $x = 26\%$–90%).[1,5]

In order to compare the catalytic properties of zeolites, a kinetic study of the reaction of methanol with hydrogen sulfide was carried out.[28,29] It was found that the rate and selectivity of

Table 2. The interaction of alcohols with hydrogen sulfide on Al_2O_3.

Alcohol	T/°C	M	τ/s	x (%)	S (%)				Ref.
					thiol	sulfide	ether	alkene	
Methanol	370	1	3	100	37	63	0	0	17
	370	10.8	3	100	88	12	0	0	17
	350	2	~6	97	50	50	0	0	14
	360	1.6	0.06	86	40	35	24	0	11
	360	0.6	0.2	85	6	81	12	0	12
Ethanol	317	2.9	5.6	93	46	2	13	39	3
	350	4.5	~7.3	99	78	–	–	–	18
1-Propanol	290	2	0.1	< 10	15	0	32	20	5
1-Butanol	300	10	0.12	100	36	0	0	64	15
1-Octanol	317	7.7	7.2	100	34	0	–	7	4
2-Propanol	300	5	0.14	–	< 5	–	–	–	19

the process depend on the degree of conversion of methanol ($x = 20\%-90\%$) and the concentrations of the reactants in the range 38 vol%–62 vol%. The activity and selectivity series for the zeolites investigated were established. For example, at 360 °C, $x = 50\%$, and $M = 0.6$ and 1.6, the rate of conversion of methanol (w/mmol g^{-1} h^{-1}; the first figure in brackets corresponds to $M = 0.6$ and the second corresponds to $M = 1.6$) varies in the sequence:

$$\text{HZSM-5}\,(175;\ 280) > \text{HNaY}\,(61;\ 92) > \\ > \text{NaX}\,(27;\ 52) > \text{NaY}\,(3;\ 7)\ .$$

The selectivities of these catalysts are presented below.

Catalyst	NaX	NaY	HNaY	HZSM-5
S_{MeSH} (%)	60–88	69–76	8–16	5–20
S_{Me_2S} (%)	36–24	38–12	32–36	86–80

The authors[28,29] explained the characteristic features of the variation of the catalytic properties as a function of the composition of the zeolites by the difference between the acid–base characteristics of the catalyst surfaces. The strength and concentration of the active centres of zeolites and other catalysts (Table 3) have been determined[11,12,29–32] by analysing the IR spectra of adsorbed probe molecules. Ammonia and pyridine were used in testing the proton centres, carbon monoxide was used in testing the Lewis acid centres, and deuteriochloroform was used in testing the basic centres.[33] On the basis of the data presented in Table 3, the authors[28,29] explained the high activity of the decationated zeolites and their selectivity with respect to dimethyl sulfide by the high content of strong acid centres on the surface. The reduced activity of NaX compared with the decationated forms of the zeolites (by a factor of 2–10 under the given conditions) is attributed to the difficulty of activating methanol on a surface lacking strong acid centres. The high selectivity with respect to methanethiol is due to the occurrence on paired centres (sodium cations–lattice oxygen atoms adjoining the cation) of the dissociative chemisorption of hydrogen sulfide with formation of reactive thiyl groups. The reduced activity of NaY compared with NaX is explained by the lower content in NaY of the nonlocalised Na^+ cations, which play an important role in the activation of hydrogen sulfide. However, the reaction mechanisms on NaX and NaY are the same, so that the selectivities in the formation of methanethiol and dimethyl sulfide are similar on both catalysts.

The activity of alkaline forms of zeolites has also been investigated.[25,26] An increased selectivity with respect to methanethiol (70%–90%) and a low selectivity with respect to dimethyl sulfide (5%–15%) have been observed not only on NaX (350 °C, $M = 1-4$, $\tau \approx 6$ s, $x = 30\%-80\%$) but also when a proportion of the sodium in the zeolite has been replaced by Li, K, or Cs. Under the conditions indicated, the same zeolites accelerate the reaction of hydrogen sulfide with ethanol: for $x = 47\%-82\%$, the selectivity is 17%–70% with respect to ethanethiol and 0%–6% with respect to diethyl sulfide; ethene is also formed, the selectivity with respect to this substance amounting to 24%–83%.[24,27,34] It has been found[35] that the interaction of ethanol with hydrogen sulfide on the NaX, NaY, CaX, HY, and Ln/Y (a type Y zeolite containing lanthanide elements), zeolites leads to the formation of only ethanethiol (350 °C, $P = 0.6-3.0$ MPa, $x \leqslant 5\%$). The rate of reaction (w/mmol g^{-1} s^{-1}) varies in the following sequence:

$$\text{HY}\,(1.12) > \text{Ln/Y}\,(0.89) > \text{CaX}\,(0.31) > \\ > \text{NaY}\,(0.24) > \text{NaX}\,(0.15)\ .$$

Since the activity increases on passing from cation-containing to decationated forms of zeolites, it was concluded[35] that the reaction proceeds via an ionic mechanism and is facilitated in the presence of proton centres on the surface.

In terms of the activity in the reaction involving the formation of ethanethiol from methanol and hydrogen sulfide, the zeolites can be arranged in the sequence

$$\text{LiNaX} < \text{NaX} < \text{CsNaX} < \text{KNaX}\ ,$$

Table 3. The acid–base properties of catalysts.[11,12,29–32]

Catalyst[a]	Strength of centres/kJ mol^{-1}[b] (concentration of centres/μmol m^{-2})		
	proton centres	Lewis acid centres	basic centres
HNaY	⩽ 1200 (0.2)	45–55 (0.1)	800–900 (1.0)
HZSM-5	1180 (0.4)	41–55 (0.1)	800–900 (1.1)
NaX	–	20 (3)[c]	800–900 (0.3)
MgO	1560	16 (3.9)[c]	930 (0.7)
SiO_2	1390 (2.8)	–	< 800
30% H_3PO_4/SiO_2	1300 (1.2)	–	< 800
7.5% $H_4SiW_{12}O_{40}/SiO_2$	⩽ 1180 (1.0)	–	< 800
2.3% Cr_2O_3/SiO_2	< 1300 (0.25)	28 (0.4)[c]	800 (2.0)
7% WO_3/AlSi	< 1300 (0.74)	56 (0.62)	–
γ-Al_2O_3	1420	34 (2.3); 41 (0.2)	800–900 (4.0)
η-Al_2O_3	–	34 (1.6); 56 (0.1)	800–900
2.3% Cr_2O_3/Al_2O_3	< 1300 (0.15)	36 (2.4)	900 (2.8)
8.5% WO_3/Al_2O_3	< 1300 (0.1)	36 (1.4)	800–900 (1.3)
3% HF/Al_2O_3	1310 (0.25)	42 (2.0)	< 800 (2.4)
20% K_2CO_3/SiO_2	–	< 20[c]	830–930 (2.4)
20% K_2WO_4/SiO_2	–	< 20[c]	830–900 (1.83); 950 (1.2)
5.2% KOH/Al_2O_3	–	29 (1.3)	850 (2.2); 930–950 (1.4)
6.4% K_2CO_3/Al_2O_3	–	29 (1.6)	860 (2.4); 925–950 (1.4)
3.7% $NaOH/Al_2O_3$	–	28 (1.1)	860 (1.8); 930–950 (1.2)
15% K_2WO_4/Al_2O_3	–	31 (0.5)	800–900 (2.9); 925 (0.71)
5% $NaOH/Al_2O_3$	–	20 (1.4)	850–915 (2.3); 920–960 (1.5)

[a] The content of promoting agents is indicated in mass%.
[b] A dash indicates the absence of centres.
[c] The presence of the Lewis acid centre is due to the presence of sodium, magnesium, chromium, and potassium cations (Al^{3+} in the remaining cases).

which reflects the increase in the electronegativity of the cations on passing from lithium to potassium. It has been suggested that the cations play the role of active centres activating hydrogen sulfide and participating in the formation of acid hydroxy-groups, which are necessary for the activation of the alcohols.[24]

The reaction of ethanol with hydrogen sulfide is accelerated by the $M^{2+}NaX$ (M = Cd, Zn, Ni, Co, Mn) zeolites.[36,37] The yield of the sulfur-containing product depends on temperature and the ratio $H_2S : C_2H_5OH$. Thus on ZnNaX at 300 °C, $M = 2$, $\tau \approx 6$ s, and $x = 100\%$, the selectivity is 20% in the formation of ethanethiol and 80% in the formation of diethyl sulfide, whilst at 350 °C and $M = 1$ the selectivities are 7% and 40% respectively. The reaction is complicated by the dehydration of ethanol with formation of ethene. It is believed[36,37] that the active centres in the $M^{2+}NaX$ system in the conversion of ethanol into the thiol are the acid OH groups arising from dissociative chemisorption of hydrogen sulfide on the cations and the basic centres coupled with them. The selectivity in the formation of diethyl sulfide increases with increase in the strength of the proton centres:

$$CdNaX > ZnNaX > CoNaX \gg NiNaX \gg MnNaX .$$

The ethanol dehydration side reaction occurs with participation of the acid–base centres of the $M^{2+}NaX$ zeolite.

The interaction of 1-propanol with hydrogen sulfide on NaX leads to the formation of propane-1-thiol in 10%–20% yield with a small amount of ethanethiol and dimethyl sulfide (350 °C, $\tau \approx 6$ s, $M = 1-4$). On NaY, the yield of propane-1-thiol under these conditions is less than 2 mol%. The thiolation reaction is accompanied by the decomposition of 1-propanol with formation of propene.[27] In the interaction of 1- and 2-propanols with hydrogen sulfide on the $M^{2+}NaX$ (M = Cd, Zn, Ni, Co, Mn) zeolites, the dehydration of the alcohol with formation of propene predominates. The overall selectivity with respect to the thiol and the sulfide (with the former predominating) is 2%–36% (350 °C, $M = 1-4$, $x = 10\%-90\%$).[27,38] It is suggested that the acid OH groups and the cationic centres of the zeolites participate in the thiolation process. At a high concentration of strong proton centres on the zeolite surface, the contribution of the alcohol dehydration side reaction increases.

The interaction of 1-butanol with hydrogen sulfide has been investigated[15] in the presence of the NaX zeolite. The reaction products are butane-1-thiol and butenes, which are formed with selectivities of 40% and 60% respectively (300 °C, $M = 10$, $\tau = 0.4-2.1$ s, $x = 27\%-83\%$).

Table 4. Synthesis of alkanethiols from alcohols and hydrogen sulfide in the presence of cationic forms of zeolites.

Alcohol	Zeolite	T/°C	M	τ/s	x (%)	Yield of alkanethiol (mol%)	Ref.
Methanol	NaX	350	4	~6	85	65	24, 25
	NaX	360	1.6	4.2	80	66	29
	KNaX	350	2	~6	80	71	25
	NaY	350	4	~6	50	30	25, 26
	NaY	360	1.6	8.4	64	40	29
Ethanol	NaX	350	4	~6	95	74	34
	KNaX	350	2	~6	82	52	24
	CdNaX	250	2	~6	85	21	36
	NiNaX	300	2	~6	76	28	36
1-Propanol	NaX	350	4	~6	70	20	27
	CdNaX	250	4	~6	80	23	38
2-Propanol	CdNaX	250	4	~6	80	10	38
1-Butanol	NaX	300	10	21	83	35	15

Thus dialkyl sulfides are formed under the influence of various forms of zeolites, their cationic forms being more suitable for the synthesis of alkanethiols. The highest attained experimental yields of alkanethiols are indicated in Table 4.

3. Supported catalysts

From the practical point of view, it is preferable to use catalysts obtained by depositing the active components on a carrier, since this involves a smaller consumption of the active substance, a high degree of its dispersion is attained, and thermal stability of the catalyst is ensured. This was already noted in an early study,[7] the authors of which established that ThO_2 deposited on pumice is preferable to the massive oxide. Catalysts consisting of the oxides, sulfides, and salts of Group 1–6 and 8 elements deposited on aluminium oxide, silicon dioxide, aluminosilicate, pumice, and carbon have been mentioned in patents (see the relevant reviews[2–8]). In the later studies considered in the present review, the supported catalysts for the conversion of alcohols into thiols were compared quantitatively, in many instances on the basis of kinetic investigations, and the relations between the catalytic and acid–base properties of the catalysts were deduced.

a. Acid catalysts

The catalysts obtained by modifying SiO_2 with phosphoric and sulfuric acids as well as the carrier itself exhibit a low activity in the reaction of methanol with hydrogen sulfide. Thus, on the H_3PO_4/SiO_2 specimens, the degree of conversion of methanol was less than 1% and sulfur-containing products were not formed (350 °C, $M = 0.5-2.0$, $\tau \approx 10$ s).[14] On the 30% H_3PO_4/SiO_2 catalyst at 360 °C, $M = 1$, and $\tau \approx 25$ s, the selectivities with respect to methanethiol and dimethyl sulfide were 1% and 10% respectively for a rate of consumption of methanol of 5 mmol g^{-1} h^{-1}, whilst after the increase in τ to 42 s and for $M = 0.6$, the degree of conversion x reached 100% and the selectivity with respect to dimethyl sulfide was 25%.[11,12] According to the authors[11,12] the activity of catalysts of this type is determined by the presence on the surface of proton centres, but the low acidity of H_3PO_4/SiO_2 as well as the low acidity of SiO_2 (Table 3) made the thiolation reaction ineffective.

It has been established[19] that hydrogen sulfide reacts with an alcohol at an elevated pressure on the H_3PO_4 (50 mass%–85 mass%)/kieselguhr catalyst, but the isomeric thiol is then formed preferentially. For example, instead of propane-1-thiol, propane-2-thiol is formed from 1-propanol is 41% yield (276 °C, $P = 0.9-1.0$ MPa, $M = 6$, $\tau = 0.14$ s); in the interaction of hydrogen sulfide with 1-dodecanol, only dodecane-2-thiol was obtained (350 °C, $P = 1.2$ MPa, $M = 4$); on interaction with hydrogen sulfide, 2-propanol, 2-butanol, and 2-pentanol are converted into the corresponding alkane-2-thiols in 37%–63% yields (175–300 °C, $P = 0.9-1.0$ MPa, $M = 4-5$, $\tau \approx 0.14$ s).[19]

Heteropolyacids with a Keggin type anion, such as silicotungstic acid $H_4SiW_{12}O_{40}$ (HSiW) and phosphotungstic acid $H_3PW_{12}O_{40}$ (HPW), deposited on silicon dioxide and containing very strong proton centres on the surface, were found to be more effective in the reaction of methanol with hydrogen sulfide[11,13] (Table 3). Thus the selectivities with respect to methanethiol and dimethyl sulfide on the 7.5% $HSiW/SiO_2$ catalyst at 360 °C, $M = 1.6$, and $x = 80\%$ were 49% and 51% respectively. The increase in the HSiW concentration to 25 mass% leads to an increase in the selectivity with respect to dimethyl sulfide to 80%. On the 30% HPW/SiO_2 catalyst, the selectivities under the conditions indicated were 70% with respect to methanethiol and 24% with respect to dimethyl sulfide, which differs from the results obtained on massive HPW, where the selectivities with respect to methanethiol and dimethyl sulfide were 16% and 64% respectively. The increase almost by an order of magnitude in the activity of the deposited heteropolyacid compared with SiO_2 and H_3PO_4/SiO_2 can be explained by the increased proton acidity. The different selectivities in the formation of thiolation products on the deposited and massive

Table 5. The activities and selectivities of supported acid catalysts in the reaction of methanol with hydrogen sulfide at 360 °C, $x = 80\%$, and a methanol concentration of 38–62 vol%.[11,12,30]

Catalyst	$M = 0.6$			$M = 1.6$		
	w/mmol $g^{-1}h^{-1}$	S (%)		w/mmol $g^{-1}h^{-1}$	S (%)	
		methanethiol	dimethyl sulfide		methanethiol	dimethyl sulfide
$HSiW/SiO_2$	–	–	–	21	49	51
Cr_2O_3/SiO_2	5	40	60	–	–	–
WO_3/SiO_2	12	23	74	21	46	43
WO_3/AlSi	–	–	–	102	43	49
γ-Al_2O_3	340	15	54	637	37	35
Cr_2O_3/Al_2O_3	460	10	80	832	22	50
MoO_3/Al_2O_3	330	20	70	767	53	47
V_2O_5/Al_2O_3	400	40	40	661	54	31
WO_3/Al_2O_3	214	2	70	547	51	37
HF/Al_2O_3	307	4	20	1338	34	51
B_2O_3/Al_2O_3	–	–	–	554	41	47
H_2SO_4/Al_2O_3	–	–	–	612	37	38

HPW are due to the decrease in the strength of the proton centres of the heteropolyacid on the carrier. However, in the reactions of hydrogen sulfide with higher alcohols, the heteropolyacids are relatively ineffective catalysts. Thus the HPW/SiO_2 catalyst as well as massive HPW are almost inactive in the reaction of 2-propanol with hydrogen sulfide:[38] at 250 °C, $M = 4$, $\tau \approx 6$ s, the degree of conversion of the alcohol being less than 1%. Only the dehydration of the alcohol with formation of but-1-ene and but-2-ene takes place in the reaction of hydrogen sulfide with 1-butanol on the 25% $HSiW/SiO_2$ specimen (300 °C, $M = 10$, $\tau = 0.04-5.40$ s, $x = 38\%-100\%$).[15]

The reaction of methanol with hydrogen sulfide is accelerated by transition metal oxides deposited on SiO_2 or AlSi and having on their surfaces strong proton centres, weak Lewis acid centres, and moderately strong basic centres (Table 3). The catalytic properties of these specimens differ little from that of the proton-donor $HSiW/SiO_2$ catalyst (Table 5).

By varying the reaction conditions (360 °C, $M = 0.6-1.6$, $\tau = 4-7$ s, $x = 80\%-95\%$) in the presence of chromium, molybdenum, and tungsten oxides deposited on SiO_2, it was not possible to obtain methanethiol and dimethyl sulfide in yields exceeding 40 mol% and 60 mol% respectively.[11,12] Higher alcohols react with hydrogen sulfide with difficulty. Thus, even in the presence of an excess of hydrogen sulfide, 1-butanol is converted on Cr_2O_3/SiO_2 into butane-1-thiol and butenes, the selectivities in the formation of which amount to 20% and 80% respectively (300 °C, $M = 10$, $\tau = 0.36-7.90$ s, $s = 20\%-92\%$).[15]

The reaction of methanol with hydrogen sulfide has been investigated[11,12] on catalysts obtained by introducing acid additives (boric, sulfuric, and hydrofluoric acids and the Cr, V, Mo, and W acid oxides) into Al_2O_3. The selectivities of the above catalysts were close to that of the $HSiW/SiO_2$ acid catalyst, but their activities were 25–50 times higher than that of the latter. In terms of their catalytic properties, the acid aluminium oxide catalysts do not differ greatly from pure aluminium oxide. Certain data on this point are presented in Table 5. According to the authors,[11,12] this is due to the similarity of the acid–base characteristics of their surfaces. It follows from Table 3 that the Al_2O_3 surface contains strong Lewis acid centres and moderately strong basic centres, weak proton centres also being present. The modification of Al_2O_3 by acid additives leads to an increase in the strength of the Lewis acid centres, arising due to the presence of Al^{3+}, a decrease in the basicity of the specimen, and also the appearance of strong proton centres; it may be that weak Lewis acid centres (cations) may also function as active centres on the surfaces of specimens containing chromium, molybdenum, and tungsten oxides on Al_2O_3.

An increase in the acidity of aluminium oxide catalysts leads to an increase in the rate of conversion of methanol per gram of the catalyst.[11,12] The rate of reaction, referred to a single Lewis acid centre, increases with increasing strength of these centres. A decrease in the basicity of the catalyst, for example as a result of the introduction of hydrofluoric acid into Al_2O_3, reduces the selectivity for the formation of the products of the reaction involving the conversion of methanol into the thiol and promotes the formation of dimethyl ether (360 °C, $M = 0.6$, $x = 80\%$).

With increase in the content of transition metal oxides on Al_2O_3, the activity of the catalyst also increases, whilst the selectivity changes little. It follows from the results of the above studies[11,12] that acid aluminium oxide catalysts are insufficiently selective with respect to methanethiol: in the presence of chromium, molybdenum, and tungsten oxides as well as sulfuric, hydrofluoric, and boric acids deposited on Al_2O_3, the yield of methanethiol obtained from methanol and hydrogen sulfide does not exceed 50 mol% (360 °C, $M = 1.6$, $\tau = 0.12-1.10$ s, $x = 80\%-100\%$). On the other hand, dimethyl sulfide is formed selectively on these catalysts, the yield amounting to 80 mol% – 95 mol% (360 °C, $M = 0.6$, $\tau = 0.5-3.0$ s, $x = 80\%-100\%$).

It has been found[39] that, among the catalysts containing Cu, Cr, Co, Ni, Th, and Mg oxides on Al_2O_3, the specimens modified with 0.11 mass% of chromium or 0.22 mass% of copper are the most effective as regards the formation of dimethyl sulfide from methanol and hydrogen sulfide; in their presence, the yield of dimethyl sulfide is 90 mol%–97 mol% and that of methanethiol is 2 mol%–3 mol% (400 °C, $M = 0.6$, $\tau = 6.2$ s).

The reactions of hydrogen sulfide with methanol homologues on acid aluminium oxide catalysts have been investigated to a lesser extent. The reaction involving the conversion of 1-propanol into the thiol on the 3.7% WO_3/Al_2O_3 catalyst results in the formation of propane-1-thiol, propene, and dipropyl ether with selectivities of 24%–29%, 13%–17.5%, and 26.7%–31.5% respectively (250–270 °C, $M = 4.7$, $\tau = 0.1-2.0$ s, $x \leqslant 10\%$).[40] In the presence of Al_2O_3 modified by titanium and zirconium oxides, the yield of dodecane-1-thiol, obtained from 1-dodecanol and hydrogen sulfide at 200–400 °C, did not exceed 12 mol%.[22] Massive HPW, which is inactive in the conversion of 1-propanol into the thiol, became active after its deposition in an amount of 16 mass%–44 mass% on δ-Al_2O_3: the yields of propane-1-thiol and propane-2-thiol from 1- and 2-propanols reached 20 mol% (250 °C, $M = 4$, $\tau \approx 6$ s, $x = 35\%-75\%$).[38] However, it may be that the activity of this catalyst is only partly associated with the presence of the heteropolyacid, since the latter decomposes on contact with the carrier.[30]

b. Basic catalysts

The modification of the carrier by alkali metal compounds leads to the formation of catalysts with a reduced activity, a low selectivity with respect to the dialkyl sulfide, but with a high selectivity in the formation of the alkanethiol. This was already noted in early studies devoted to the conversion of methanol into the thiol.[2-4,8] Under identical conditions (400 °C, $M = 2$, $\tau = 5.5$ s, $x = 70\%-80\%$), the selectivity in the formation of methanethiol on the alkali-modified aluminium oxide is 1.2 times higher than on the unpromoted Al_2O_3, while the selectivity with respect to dimethyl sulfide is lower by a factor of 2.4. Similar changes occur in the reactions of hydrogen sulfide with ethanol (400 °C, $M = 2$, $\tau = 5.6$ s, $x = 70\%-90\%$) and with 1-octanol (317 °C, $M = 2.9$, $\tau = 5.6$ s, $x = 83\%-91\%$): the selectivity with respect to the alkanethiol on the alumina–potassium tungstate specimen is higher by a factor of 1.4–2.3 than on pure Al_2O_3, while the selectivity with respect to the dialkyl sulfide is significantly lower.[4] In the reaction of 1-propanol with hydrogen sulfide, aluminium oxide with added potassium or sodium oxide is an order of magnitude less active than pure Al_2O_3; the selectivities for the formation of propane-1-thiol are 15% and 34%–80% respectively on pure Al_2O_3 and on the oxide modified by various amounts of alkalies (290 °C, $M = 2$, $x \leqslant 10\%$).[40]

The interaction of methanol with hydrogen sulfide on carriers modified by potassium or sodium hydroxide, carbonate, and tungstate has been studied in detail.[31,41-45] The rate of conversion of methanol and the selectivity with respect to dimethyl sulfide on these catalysts are low, while the selectivity with respect to methanethiol is high. The activity of the catalysts may be due to the presence on their surfaces of definite numbers of acid–base centres. In contrast to SiO_2, which contains mainly weak proton centres, in the SiO_2 with added potassium compounds there are no proton centres—weak Lewis acid centres (apparently alkali metal cations) and strong basic centres are present (Table 3). Compared with pure silicon dioxide, the activity of the alkaline specimen at 360 °C is higher by a factor of 1.5–4.0, the selectivity with respect to methanethiol has increased from 25% to 70%–98%, while the selectivity with respect to dimethyl sulfide remains low (2%–15%). The promoting effect of the alkaline additive to SiO_2 is higher, the higher the potassium or sodium content of the silicon dioxide. For the same atomic content of potassium, the activity of, for example, K_2CO_3/SiO_2 is twice as high as that of K_2WO_4/SiO_2, but methanethiol is formed somewhat more selectively on the tungstate specimen.

The acid–base characteristics of aluminium oxide also change after the introduction of an alkaline additive (Table 3): the number of the weak proton centres present in the Al_2O_3 diminishes or they vanish altogether, the concentration and strength of the Lewis acid centres (Al^{3+}) decrease, and weak Lewis acid centres (alkali metal cations) probably also appear. Furthermore, together with the moderately strong basic centres present in the Al_2O_3, a large number of strongly basic centres are generated.

The introduction of alkaline additives into Al_2O_3 increases the activity of the catalyst in the conversion of methanol into the thiol to a greater extent than their introduction into the SiO_2. This is due to the presence on the surfaces of the aluminium oxide specimens of Al^{3+} ions, which are stronger Lewis acid centres than alkali metal cations.

The change in the acid–base properties of Al_2O_3 when the latter is modified by alkali leads, in its turn, to a change in the catalytic properties. Thus the introduction of an alkaline additive into Al_2O_3 lowers the activity with respect to methanethiol by 1–1.5 orders of magnitude and that with respect to dimethyl sulfide by 2–4 orders of magnitude compared with pure Al_2O_3. The selectivity with respect to methanethiol increases accordingly from 35%–50% on Al_2O_3 to 98% on the modified catalyst, whilst that with respect to dimethyl sulfide falls sharply. The content of the alkaline additive also affects the catalytic properties: with increase in the concentration of the promoting agent, the activity and selectivity of Al_2O_3 with respect to dimethyl sulfide diminish, whilst the activity with respect to methanethiol increases.

The similarity of the acid–base properties of specimens with identical atomic contents of the alkali metal on Al_2O_3 also ensures their virtual identical activity at 360–500 °C.[31,42,45] The nature of the anion exerts a stronger influence: among the specimens containing potassium on Al_2O_3, the carbonate and tungstate specimens exhibit the highest and lowest activities respectively, but the latter are more selective with respect to methanethiol. The carbonate and hydroxide specimens exhibit an increased activity for the formation of decomposition products—methane and carbon oxides. These differences are associated with the acid–base properties of the surface. It follows from Table 3 that the KOH/Al_2O_3, $NaOH/Al_2O_3$, and K_2CO_3/Al_2O_3 specimens differ little as regards the concentration and strength of the Lewis acid centres. Very strong basic centres are also present in the carbonate and hydroxide specimens. On the other hand, the tungstate catalyst, which is most selective with respect to methanethiol,[44] contains stronger basic centres than in the above specimens. The catalytic properties are independent of the nature of the tungstate promoting agent. Thus the catalysts obtained by introducing sodium heptatungstate, dodecatungstate, metatungstate, and the normal tungstate into Al_2O_3 exhibit approximately the same activities in the reaction of methanol with hydrogen sulfide.[43] The specimen in which the alkali metal : tungsten atomic ratio is 2 : 1 exhibits the greatest selectivity with respect to methanethiol. The similarity of the catalytic properties of the specimens obtained by impregnating Al_2O_3 with solutions of the monomeric normal tungstate and by different polynuclear oxo-complexes of tungsten is a consequence of the formation of similar surface compounds.

The conversion of methanol homologues into thiols in the presence of Al_2O_3 modified by alkaline additives takes place at a lower temperature. The selectivity in the formation of alkanethiols from primary alcohols is fairly high (80%–90%) even for a high degree of conversion of the alcohol, but diminishes when secondary alcohols are converted into thiols, since this is accompanied by side reactions involving the formation of alkenes, ethers, etc. Thus in the interaction of ethanol with hydrogen sulfide on 10% K_2WO_4/Al_2O_3, the selectivities with respect to ethanethiol and diethyl sulfide are 93%–78% and 2.5%–3.6% respectively (290–382 °C, $M = 2$, $x = 60\%-83\%$).[4] In the interaction of 1-octanol with hydrogen sulfide on the same catalyst, the selectivity for the formation of octane-1-thiol is 99%–74% (235–318 °C, $M = 7.7$, $x = 48\%-100\%$); the reaction is accompanied by the formation of an alkene.[4] In the reaction of 1-butanol with hydrogen sulfide on potassium-modified Al_2O_3, the selectivity with respect to butane-1-thiol was 92%–98%, but-1-ene being formed as a side product (300 °C, $M = 10$, $\tau = 1.2-12.1$ s, $x = 30\%-95\%$).[15] The reaction of 1-dodecanol with hydrogen sulfide on the K/Al_2O_3 catalyst afforded dodecane-1-thiol with a selectivity of 47%–82%, a selectivity of 7%–42% with respect to dodecene, and a selectivity of 2%–33% with respect to the sum of dodecyl ether and dodecyl sulfide [(300–350) °C, $M = 2.6-24.0$, $\tau = 0.04-2.50$ s, $x = 15\%-100\%$].[46] 2-Butanol, a secondary alcohol, is largely dehydrated in hydrogen sulfide on the catalysts indicated above with formation of butene; among the sulfur-containing substances, only butane-2-thiol is formed with a selectivity of 11%–26% (275–300 °C, $P = 0.1-0.3$ MPa, $M = 4$, $\tau = 0.3-0.9$ s, $x = 59\%-71\%$).[47]

Thus the composition of the catalysts exerts a considerable influence on the rate of the interaction of alcohols with hydrogen sulfide and on the mode of the reaction. By varying the type of the acid–base centres and their numbers on the surface, it is possible to obtain an active and selective catalyst for the formation of the thiol. Deliberate search for such catalysts is facilitated when the reaction mechanism is known.

III. The mechanism of conversion of alcohols into thiols by hydrogen sulfide

1. Routes to the formation of the reaction products

Knowledge of reaction paths is important for the regulation of the process selectivity. This problem has been elucidated in greatest detail for the interaction of methanol with hydrogen sulfide.

It has been postulated[25,26,28,29] that the products of the thiolation of methanol and dimethyl ether are formed from methanol by independent paths on the NaX, NaY, HNaY, and HZSM-5 zeolites. In a number of instances, for example on AlSi and γ-Al_2O_3 (both pure and modified by HF and B_2O_3), the selectivity in the formation of dimethyl ether for low degrees of conversion of methanol was much higher than the overall selectivity with respect to methanethiol and dimethyl sulfide.[11,12,17] This justified the conclusion that the latter are formed as a result of the interaction of hydrogen sulfide with dimethyl ether produced on dehydration of methanol.

The routes to the formation of methanethiol and dimethyl sulfide may differ. It has been suggested[25,26,29] that they are obtained via independent paths on zeolites. However, the view that dimethyl sulfide is a secondary product arising from methanethiol predominates.

The most reliable conclusions concerning the routes to the formation of the products from methanol and hydrogen sulfide on different catalysts have been reached on the basis of kinetic studies.[11,12,30,31,45,48,49] The primary oxygen-containing product arising from methanol is its dehydration product — dimethyl ether:

$$2\,CH_3OH \rightleftharpoons (CH_3)_2O + H_2O\,.$$

Dimethyl ether as well as the initial methanol can decompose with formation of carbon oxides and methane.[50] The increase in selectivity with respect to methanethiol with decrease in the degree of conversion of methanol permitted the conclusion that methanethiol is the primary sulfur-containing product of the interaction of methanol with hydrogen sulfide:

$$CH_3OH + H_2S = CH_3SH + H_2O\,.$$

However, the reaction of hydrogen sulfide with dimethyl ether is also possible:

$$(CH_3)_2O + H_2S = CH_3SH + CH_3OH\,.$$

For example, it may occur on Al, K, W, and Mo oxides and sulfides.[2,4,45,48,49,51,52] The rates of reaction of methanethiol and dimethyl ether and also the selectivities in the formation of methanethiol with hydrogen sulfide under similar conditions are comparable.[45,48,49] Hydrogen sulfide is consumed in the reaction with methanol on different catalysts only in the formation of methanethiol and dimethyl sulfide and the degree of its conversion is therefore equal to the overall yield of these products.

Methanethiol, formed from hydrogen sulfide and methanol, can undergo various reactions, in particular reactions involving the formation of dimethyl sulfide. The formation of the latter from methanethiol is indicated by a series of experimental facts.[45,49,53] Thus the selectivity with respect to methanethiol decreases and that with respect to dimethyl sulfide increases with increase in the degree of conversion of the reactants (methanol, dimethyl ether, hydrogen sulfide). When methanethiol is added to the initial reaction mixture, the rate of formation of dimethyl sulfide increases. Indirect evidence is provided also by the occurrence on the catalysts accelerating the interaction of methanol with hydrogen sulfide of the selective reaction involving the synthesis of dimethyl sulfide by the decomposition of methanethiol in helium or of the reactions of methanethiol with methanol or dimethyl ether. However, although the selectivity with respect to dimethyl sulfide in the above reactions increases with increasing degree of conversion of the reactants, it does not reach 100% even for the total conversion of the latter, which is associated with the occurrence of a reversible reaction of dimethyl sulfide with hydrogen sulfide. The catalysts active in the reaction of methanol with hydrogen sulfide or methanethiol accelerate the above interaction as well.[54,55] The experimental data presented demonstrate that the following reactions take place involving methanethiol:

$$CH_3SH + CH_3OH = (CH_3)_2S + H_2O\,,$$

$$CH_3SH + (CH_3)_2O = (CH_3)_2S + CH_3OH\,,$$

$$2\,CH_3SH \rightleftharpoons (CH_3)_2S + H_2S\,.$$

For a long contact time and at an elevated temperature, methanethiol and dimethyl sulfide are partly decomposed with formation of methane and the deposition of coke on the surface.[54]

Thus the products of the interaction of methanol with hydrogen sulfide may be formed as a result of the occurrence of the reactions listed below on various catalysts, the composition of which influences only the rates of individual stages. The dehydration of methanol leads to the formation of dimethyl ether. The reaction of methanol with hydrogen sulfide or possibly with dimethyl ether affords methanethiol, which is converted into dimethyl sulfide either by reacting with a second molecule of methanol or dimethyl ether or by disproportionating. The partial decomposition of dimethyl ether and methanol leads to the formation of carbon monoxide and methane. The latter is also a product of the degradation of methanethiol and dimethyl sulfide.

In the conversion of higher alcohols into thiols, additional reaction paths appear — the decomposition of the initial alcohol and of the sulfur-containing products formed from it. In the interaction of hydrogen sulfide with ethanol and 1- and 2-propanols on zeolites, both decationated and in the sodium-form, the principal reaction products are the corresponding thiols and an alkene. The occurrence of the consecutive reactions,

$$RCH_2CH_2OH \xrightarrow[-H_2O]{} RCH{=}CH_2 \xrightarrow{H_2S} RCH_2CH_2SH\,,$$

has been suggested.[27,36] The alcohol is dehydrated with formation of an alkene, which then reacts with hydrogen sulfide to produce the thiol. However, the authors do not rule out also the possibility of the parallel formation of the thiol and the alkene.

$$RCH_2CH_2OH \begin{cases} \xrightarrow{H_2S} RCH_2CH_2SH \\ \xrightarrow[-H_2O]{} RCH{=}CH_2 \end{cases}$$

According to the authors,[27,36] a small amount of ethanethiol and dimethyl sulfide is formed in this reaction when hydrogen sulfide interacts with the propanol decomposition products.

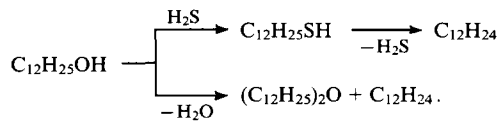
Kinetic study[5] led to the conclusion that, in the presence of Al_2O_3, 1-propanol reacts via three independent paths in hydrogen sulfide:

$$C_3H_7OH \begin{cases} \xrightarrow{-H_2O} C_3H_8\,, \\ \xrightarrow{-H_2O} (C_3H_7)_2O\,, \\ \xrightarrow{H_2S} C_3H_7SH\,. \end{cases}$$

The reaction of hydrogen sulfide with 1-butanol on the NaX, MgO, Al_2O_3, and Cr_2O_3/SiO_2 catalysts does not lead to the formation of dibutyl ether and dibutyl sulfide, only butane-1-thiol and butenes (mainly but-1-ene) being produced. The selectivity with respect to the latter compounds is independent of the degree

of conversion of butanol.[15] On the grounds of these findings, it is suggested that the 1-butanol conversion products, like those obtained from 1-propanol,[5] are obtained via independent routes from the initial alcohol. However, bearing in mind the high rate of the decomposition of alkanethiols and dialkyl sulfides compared with alcohols[27,46,56] and its increase with increasing molecular mass,[57-59] one cannot rule out the possibility that butenes appear on decomposition not only of the alcohol but also of the products of its thiolation.

The routes to the formation of the products of the reaction of 1-dodecanol with hydrogen sulfide on the alkali-modified aluminium oxide have been investigated.[56] The main products are dodecane-1-thiol and dodecene, the overall yield of dodecyl ether and dodecyl sulfide not exceeding 5 mol%. The selectivity with respect to dodecane-1-thiol remains approximately constant at $x \leqslant 60\%$, decreasing at higher degrees of conversion. This is owing to the fact that mainly the dodecanethiol and not the initial alcohol decomposes, which is indicated by the form of the variation of the selectivity in the formation of the 1-dodecanol conversion product, by the increased yield of dodecene when dodecane-1-thiol is added to the initial mixture, and also by data on the decomposition of 1-dodecanol under a helium atmosphere and of dodecane-1-thiol in hydrogen sulfide. Mainly the consecutive process involving the formation and decomposition of dodecane-1-thiol takes place, the contribution of the parallel alcohol dehydration reaction being small:



2. Relation between the catalytic and acid–base properties

The acid–base properties of the surfaces of the catalysts influence not only their activity in the reaction of an alcohol with hydrogen sulfide to form an alkanethiol and a dialkyl sulfide (see above), but also the rates of the individual stages of the process. This has been established as a result of detailed studies of the synthesis of methanethiol or dimethyl sulfide from methanol and hydrogen sulfide and of the reactions involving the formation of dimethyl sulfide by the disproportionation of methanethiol and its interaction with methanol.[11,12,28-31,53,54,60] The results permitted the conclusion that all these reactions are accelerated by catalysts having both proton and Lewis acid centres. The activity of the catalyst per centre increases with increase in the strength of the acid centre.[11,12,60] Identical features of the variation of the activity as a function of the nature and strength of the centres are characteristic of different reactions. This is illustrated by the results, presented in Table 6, of the determinations of the activities of the catalysts in various reactions involving the synthesis of methanethiol and dimethyl sulfide. Taking into account the available data concerning the acid–base properties of the catalyst (Table 3), one may conclude that the reactions proceed under the influence of both proton and Lewis acid centres. A catalyst with weak proton centres (H_3PO_4/SiO_2) exhibits a low activity in the formation of methanethiol and dimethyl sulfide. Catalysts with strong proton centres ($HSiW/SiO_2$) have the best parameters. The activity of catalysts having weak Lewis acid centres (NaX, MgO, Cr_2O_3/SiO_2) is approximately at the same level as that of the catalysts with strong proton centres. The activity of aluminium oxide catalysts containing strong Lewis acid centres is appreciably higher than that of the catalysts with strong proton centres. For this reason, the activity of the proton-donating specimens containing even a small number of strong Lewis acid centres (decationated zeolites) is higher than the activity of a 'purely' proton-donating specimen.

The effectiveness of catalysts with strong Lewis acid surface centres is due to the presence of the basic centres associated with them, which participate in the activation of both the alcohol and hydrogen sulfide. The suppression of the basic centres, even when it is accompanied by some increase in the strength of the acid centres (for example, as a result of the introduction of hydrofluoric acid into Al_2O_3), lowers the overall activity and selectivity of the catalyst as regards the formation of the products of the thiolation reaction.[12] It has been established[11,12,28-31,53,54,60] that both the overall activity of the catalysts in all the reactions indicated and their activity in relation to the formation of dimethyl sulfide decrease with increase in the strength of the basic centres and with decrease in the strength of the acid centres (for example, when the carrier is modified by alkali). The selectivity with respect to methanethiol increases under these conditions in the reaction of hydrogen sulfide with methanol. A catalyst containing strong Lewis acid centres and moderately strong basic centres (for example Al_2O_3 modified by acid additives or a decationated high-silica zeolite) is an active and selective catalyst in the synthesis of dimethyl sulfide from methanol and hydrogen sulfide or methanethiol.

Since the type, concentration, and strength of the active centres influence the activity of the catalyst equally in all the reactions indicated above, the conclusions concerning the routes to the formation of the products of the thiolation of methanol, reached on the basis of kinetic studies, must be regarded as valid (see Section III).

The acid–base properties of the catalyst surfaces influence the rate of the reaction of hydrogen sulfide with methanol homologues and the mode of the reaction. Thus it has been established[15] that the rate of conversion of 1-butanol in an excess of hydrogen sulfide is very high on catalysts with very strong proton centres (decationated zeolite, heteropolyacid), whilst on catalysts with weakened Lewis acid centres (NaX, MgO, Cr_2O_3/SiO_2) it is much lower. Butanol is converted fastest on Al_2O_3, having strong Lewis acid centres and moderately strong basic centres. The rate of reaction increases with increase in the concentration and strength of the acid centres on the surface. Thus the rate of conversion of 1-butanol, referred to one acid centre, is higher the greater the strength of these centres. However, 1-butanol decomposes rapidly with formation of butenes on highly active acid catalysts, the rate of the process increasing with increase in the acidity of the surface. An additional amount

Table 6. The rates of formation of methanethiol and dimethyl sulfide on catalysts with different acid–base properties.

Catalyst	Rate of formation/μmol m^{-2} h^{-1}			
	of methanethiol[a]	of dimethyl sulfide		
		b	c	d
H_3PO_4/SiO_2	0.22	18	–	3
$HSiW/SiO_2$	28	30	17	34
NaX	46	10	5	10
MgO	33	–	–	20
Cr_2O_3/SiO_2	37	8	12	12
γ-Al_2O_3	715	4066	800	3200
η-Al_2O_3	1137	869	–	2000
Cr_2O_3/Al_2O_3	1126	1269	1000	2720
H_2SO_4/Al_2O_3	863	–	270	1900
$NaOH/Al_2O_3$	44	3	6	10
HNaY	8.4	24	91	8
HZSM-5	112	300	200	600

[a] Methanethiol is formed by the $CH_3OH + H_2S$ reaction: $T = 360$ °C, $[CH_3OH] = 17$ mM, $[H_2S] = 28$ mM, $x = 80\%$, $M = 1.6$.[11,29]
[b] $CH_3OH + H_2S$: $T = 360$ °C, $M = 0.6$, $[CH_3OH] = 28$ mM, $[H_2S = 17$ mM, $x = 80\%$.[11,12,29]
[c] $CH_3OH + CH_3SH$: $T = 350$ °C, $[CH_3SH] = 3.2$ mM, $[CH_3OH] = 1.7$ mM, $x = 50\%$.[53]
[d] $2CH_3SH \rightleftharpoons (CH_3)_2S + H_2S$: $T = 350$ °C, $[CH_3SH] = 2$ mM, $x = 20\%$.[60]

of butenes probably appears as a consequence of the decomposition of the sulfur-containing substances produced. The formation of the products of the thiolation reaction between 1-butanol and hydrogen sulfide is therefore hindered on acid catalysts: dibutyl sulfide was not detected at all and the selectivity with respect to butane-1-thiol was low. In the presence of catalysts with strong basic centres and weakened Lewis acid centres (for example, K/Al_2O_3), butane-1-thiol is mainly formed. The decrease in the selectivity in the formation of the products of the thiolation reaction in the presence of acid catalysts and the increase in the selectivity in the formation of an alkanethiol on basic catalysts have been observed also in the reactions of hydrogen sulfide with ethanol, 1- and 2-propanols, and 1-dodecanol.[2,3,5,24,27,36–38,46]

3. Adsorption

In considering the mechanism of the conversion of alcohols into thiols by hydrogen sulfide, it is necessary to take into account the available information about the structure and reactivity of the intermediate surface compounds arising when the reactants and their reaction products are adsorbed on the catalyst. These data have been obtained mainly by IR spectroscopic, NMR, and thermoprogrammed desorption (TPD) methods.

Alcohols may be adsorbed on the surfaces of acid–base catalysts[61,62] in the molecular form as a result of the interaction of the oxygen atom of the alcohol with a proton or Lewis acid centre of the catalyst and of the hydrogen atom of the alcoholic hydroxy-group with a basic surface centre. The decomposition of the alcohol in the molecularly adsorbed form leads to the formation of hydroxide and alkoxide groups on the surface. The latter may in addition form a hydrogen bond with the basic centres of the catalyst.

The adsorption of a dialkyl ether[63,64] on proton-donating catalysts at a low temperature leads to the appearance of a hydrogen-bonded form involving a proton catalyst centre and the oxygen atom of the ether. On catalysts with paired acid–base centres, a coordinate bond is formed between the oxygen atom of the ether and the Lewis acid centre together with an additional bond between a hydrogen atom of the alkyl group and a basic centre. At an elevated temperature, these forms decompose with formation of alkoxide groups on the surface.

In the adsorption of an alkanethiol on the surface of an acid–base catalyst, there is a possibility of the formation of an associatively bound form as a result of the interaction of the sulfur atom of the alkanethiol with an acid catalyst centre and of the hydrogen atom of the thiyl or alkyl group with a basic centre. The decomposition of the molecular form of the adsorbed thiol leads to the appearance of OH and RS groups on the surface and also to the formation of hydrogen sulfide and the alkoxylation of the surface.[1,58,65–69]

The dialkyl sulfide is adsorbed on the surface[1,65,67] with participation of different centres. At a low temperature, the sulfide is protonated at the sulfur atom by the acid OH groups on the surface; a donor–acceptor complex with participation of the sulfur atom in the sulfide is formed on Lewis acid centres; there is also a possibility of an additional bond between a hydrogen atom of the alkyl group and a basic centre. At an elevated temperature, and also at a low surface coverage, the surface complex decomposes at the C–S bond to form RS and RO groups.

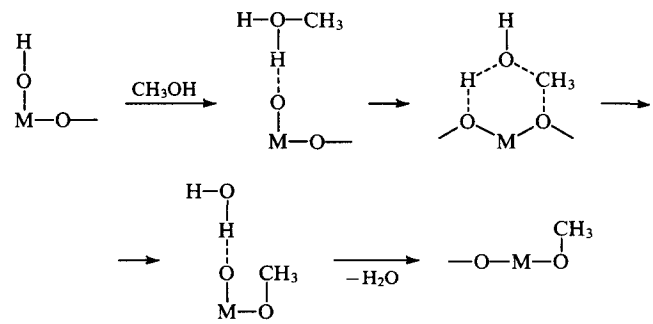
Hydrogen sulfide is adsorbed on proton-donor catalysts only via an associative mechanism:[70–74] a hydrogen-bonded form arises as a consequence of the interaction of the sulfur atom with a proton centre. On catalysts with paired Lewis acidic–basic centres, hydrogen sulfide is chemisorbed. At a reduced temperature and a high surface coverage, a donor–acceptor bond is formed between the sulfur atom and a Lewis acid centre and between a hydrogen atom of hydrogen sulfide and a basic surface centre. With increase in temperature and with decrease in surface coverage, the initial structure decomposes and acid OH groups and HS fragments are formed on the surface. There is a possibility of the dissociation of both H–S bonds in hydrogen sulfide with formation of S^{2-} groups, whereupon the concentration of the acid OH groups on the surface increases.

4. Elementary stages of the thiolation reaction

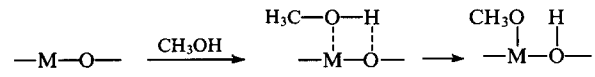
In view of the ease of the dissociative chemisorption of alcohols, the majority of investigators assumed that the thiolation reaction begins with the formation of alkoxide groups on the catalyst surface. This applies to the reactions of hydrogen sulfide with methanol on massive metal oxides and sulfides, deposited acid and alkaline catalysts, heteropolyacids, and zeolites,[11,12,25,26,28–31,75] with ethanol on the M^{2+} NaX zeolites,[36] with 1- and 2-propanols on NaX, NaY, HNaY, HZSM-5,[27] and Al_2O_3,[5] with 1-butanol on MgO, NaX, Cr_2O_3/SiO_2, K/Al_2O_3, and γ-Al_2O_3,[15] and with 1-dodecanol on K/Al_2O_3.[56]

It has been suggested[25,26,28,29] that the acid OH groups, present in the initial decationated zeolite or produced as a consequence of the dissociative chemisorption of hydrogen sulfide on the cationic forms of the zeolites, participate in the interaction of methanol with hydrogen sulfide on zeolites. However, it has been established[69,76] that methanol may be adsorbed on the sodium-forms of the NaX and NaY zeolites with participation of the sodium cation. On other catalysts, without strong proton centres on the surface (for example, the massive Al, Ti, Mg, Zr, and Ce oxides and deposited catalysts of the basic type), the coordination of methanol to the paired centres is most probable:[14,45,61] the oxygen atom of the alcohol is coordinated to a Lewis acid centre, while the hydrogen atom of the alcoholic OH group is coordinated to a basic centre. The subsequent decomposition of the associatively bound methanol leads to the methoxylation of the surface. The surface methoxide groups may react. Thus their interaction with a second alcohol molecule leads to the formation of dimethyl ether. The processes occurring on the proton and paired acid–base surface centres may be described by the following schemes (Schemes 1–3):

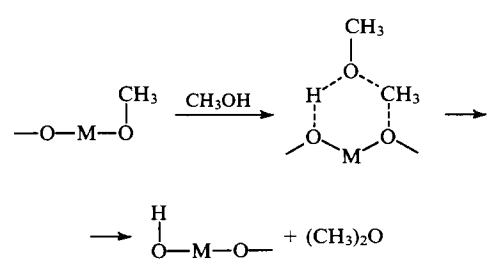
Scheme 1



Scheme 2

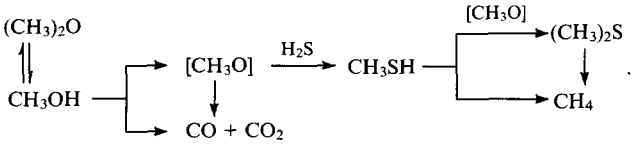


Scheme 3



As already mentioned above, dimethyl ether may react with hydrogen sulfide, affording methanethiol and dimethyl sulfide. Since the ether is readily dissociatively chemisorbed on different catalysts with formation of surface RO groups, there are no grounds for the hypothesis that methanethiol and dimethyl sulfide are formed directly from dimethyl ether. Its involvement in the formation of the thiolation products is usually accounted for by the decrease in the selectivity with respect to the ether as the degree of conversion of the alcohol increases. However, this may be a consequence not of the consumption of the ether in the formation of sulfur-containing compounds, but of the decrease in the surface concentration of the CH_3O groups interacting with hydrogen sulfide and methanethiol, which leads to a decrease in the rate of interaction of the RO groups with the alcohol.[29] The increase in the rate of conversion of methanol into the thiol, sometimes observed[77-79] in the presence of dimethyl ether, may be due to the additional methoxylation of the surface.

The following sequence of catalytic reactions with participation of methanol and hydrogen sulfide has been postulated:[45]



Both associatively[25,26,29] and dissociatively adsorbed hydrogen sulfide[45,49,80,81] may participate in the formation of methanethiol and dimethyl sulfide.

The conclusion that the thiolation reaction takes place with participation of surface methoxide groups and activated hydrogen sulfide has been confirmed by studies on the process by NMR and IR spectroscopic methods. Thus it has been found[14] that the addition of hydrogen sulfide to a SiO_2 specimen on which methanol has been adsorbed previously with subsequent heating to 350 °C leads to the disappearance of the absorption bands due to the methoxy-groups (1152 and 1044 cm^{-1}) from the IR spectrum, and to the appearance of the absorption bands of methanethiol (960 and 2845 cm^{-1}) and dimethyl sulfide (980, 1032, 1435, and 2980 cm^{-1}). The absorption bands due to methane (3017 and 1306 cm^{-1}) and the bands due to the formate structures produced on decomposition of methanol (1372, 1386, and 1583 cm^{-1}) appear under certain conditions. Similar results have been obtained on the decationated HNaY zeolite,[25,26] TiO_2, and Al_2O_3.[14] The exposure of the weakly active PO_4^{3-}/SiO_2 catalyst to hydrogen sulfide leads to some decrease in the intensity of the absorption bands due to the methoxide groups, but the high strength of the bond with the surface virtually precludes their reaction and the IR spectrum contains no absorption bands due to sulfur-containing compounds.[14]

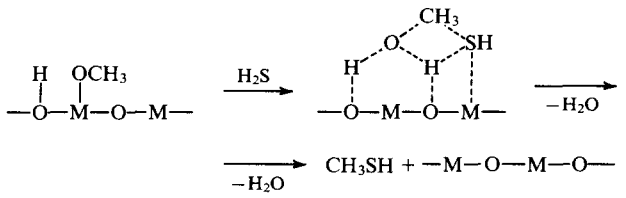
After the exposure to hydrogen sulfide of Al_2O_3 modified by potassium or sodium compounds and containing preadsorbed methanol and after heating to 200 °C, there is a decrease in the intensity of the IR absorption bands not only of the CH_3O group but also of the thiyl groups bound to Al^{3+} (in the range 2560–2580 cm^{-1}); the absorption bands due to adsorbed methanethiol and dimethyl sulfide appear simultaneously.[45]

Similar conclusions have been reached on the basis of studies of the reaction of methanol with hydrogen sulfide by the high-resolution ^1H and ^{13}C NMR methods in the solid state.[49,82] For example, when an Al_2O_3 specimen containing adsorbed methanol was exposed to hydrogen sulfide, the anisotropic line due to CH_3O ($\delta = 50$ ppm) disappeared from the ^{13}C NMR spectrum after heating above 150 °C and new lines due to dimethyl ether ($\delta = 61.9$ ppm), methanethiol ($\delta = 6.7$ ppm), and dimethyl sulfide ($\delta = 19.8$ ppm) appeared. After heating the specimen to 400 °C, the line due to methane ($\delta = -8.4$ ppm) appeared in the spectrum. On the NaX specimen, a decrease in the intensity of the signal due to the adsorbed hydrogen sulfide—molecular hydrogen sulfide ($\delta = 1.0$ ppm) and the dissociatively chemisorbed hydrogen sulfide ($\delta = -3.6$ ppm) in equilibrium with the molecular form ($H_2S \rightleftharpoons HS^- + H^+$)—was also observed.

On interaction of hydrogen sulfide with NaX on which dimethyl ether had previously been adsorbed, signals due to the methanol, methanethiol, and dimethyl sulfide formed were observed in the ^{13}C NMR spectrum and there was a simultaneous decrease in the intensity of the signal due to dimethyl ether.

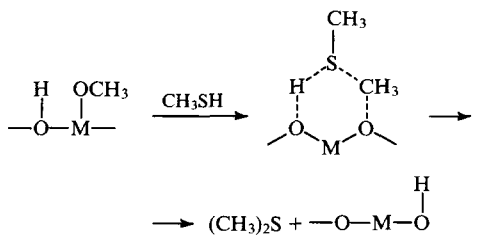
The results of the study of the conversion of methanol into the thiol on aluminium oxide catalysts made it possible to postulate the following mechanism.[45,49,80,81] When methanol interacts with a catalyst, it undergoes dissociative chemisorption, as a result of which the surface is methoxylated (Schemes 1 and 2). The interaction of the chemisorbed hydrogen sulfide with the methoxide groups leads to the formation of methanethiol (Scheme 4).

Scheme 4



The methoxide groups interact with methanethiol, activated with participation of the basic surface centres, affording dimethyl sulfide (Scheme 5).

Scheme 5

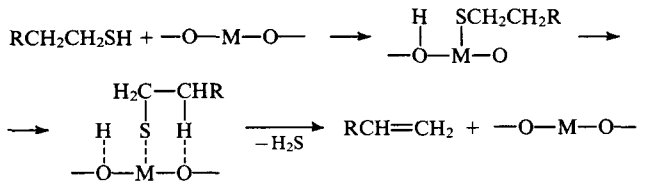


The differences between the activities and selectivites of the catalysts with respect to the formation of methanethiol depend mainly on the form in which hydrogen sulfide reacts. On proton-donor catalysts, molecular hydrogen sulfide (from the gas phase or associatively adsorbed on the surface) participates in the reaction with the CH_3O groups.[25,26,29] On catalysts with paired acid–base centres, the HS groups produced by the dissociative chemisorption of hydrogen sulfide interact with the methoxide groups, which increases the rate of formation of methanethiol. Dimethyl sulfide is formed as a result of the interaction of the CH_3O groups with the methanethiol associatively adsorbed on a basic centre, the attainment of a high rate of reaction requiring that the strength of the bond between methanethiol and the surface is optimal.[80]

The detailed mechanism of the conversion of higher alcohols into thiols has been investigated. It is believed[27,36] that in the initial stage of the reaction of hydrogen sulfide with ethanol and 1-propanol on a fresh zeolite specimen, the alcohol is dehydrated with formation of an alkene, which then reacts with the surface HS groups and is converted into the thiol; propane-2-thiol is then formed from 1-propanol. On the catalyst modified by the influence of the reaction medium, the reaction proceeds via the stage involving the interaction of hydrogen sulfide with the surface alkoxide groups, in which ethanethiol and propane-1-thiol are formed, i.e. it is postulated that the thiolation mechanism is analogous to the mechanism of the formation of methanethiol from methanol (see Scheme 4). Mashkina and coworkers[15,56] took into account the high probability of the occurrence of side reactions in the conversion of higher alcohols into thiols. In particular, the alkanethiols and dialkyl sulfides appearing on interaction of the alkoxide groups with hydrogen sulfide may be

adsorbed preferentially on the active centres, being stronger bases than the initial reactants, decomposing under these conditions with formation of alkylthio-groups (RS). An additional bond between the β-hydrogen atom of the RS group and a basic surface oxygen atom is formed on catalysts containing basic centres on the surface. As a result of the decomposition of this two-point surface complex, the alkene is eliminated. For example, the elimination of the alkene from alkanethiol is described by Scheme 6.

Scheme 6



On proton-donor catalysts without sufficiently strong basic centres, the alkene may be formed on decomposition of the hydrogen-bonded associative complex. As a result of the occurrence of similar processes, the alkene is also eliminated from the surface alkoxide groups.[77]

5. Kinetics

The validity of the postulated mechanism of the conversion of alcohols into thiols has been confirmed by the study of the kinetics of the reactions of methanol with hydrogen sulfide, of methanethiol with methanol, and of hydrogen sulfide with 1-dodecanol. A simplified mechanism, in which the formation of small amounts of CO and CH_4 is neglected and the rapid occurrence of the stages involving the chemisorption of hydrogen sulfide, the methoxylation of the surface, and the desorption of methanethiol is assumed, has been postulated for the reaction of methanol with hydrogen sulfide on acid aluminium oxide catalysts.[45,48,49,79,81] Account is also taken of the possibility that water blocks the surface (Scheme 7).

Scheme 7

$$CH_3OH + [X_1] \overset{(1)}{\rightleftharpoons} [X_2] + H_2O$$

$$H_2S + [X_2] \overset{(2)}{\rightleftharpoons} [X_1] + CH_3SH$$

$$CH_3SH + [X_2] \overset{(3)}{\rightleftharpoons} [X_1] + (CH_3)_2S$$

$$CH_3OH + [X_2] \overset{(4)}{\rightleftharpoons} [X_1] + (CH_3)_2O$$

$$H_2O + [X_1] \overset{(5)}{\rightleftharpoons} [X_3]$$

$[X_1]$, $[X_2]$, and $[X_3]$ are the initial active surface centre, the methoxylated centre, and the centre covered by water respectively.

Because of the wide distribution of the acid and basic centres on the catalyst surfaces with respect to their strength, the theoretical procedure developed by Temkin[83] for the description of the kinetics of heterogeneous-catalytic reactions occurring on a uniformly inhomogeneous surface, where the heat of adsorption varies linearly with the surface coverage by the reactants, was employed in devising the kinetic model. By assuming a high coverage of the active surface sites by water and that the rate of the process is limited by stages *2–4*, the following simplified kinetic equations were obtained:

$$w_{H_2S} = k_2^0 k P_{H_2S} P_{MeOH}^{1/2} P_{H_2O}^{-1} ,$$

$$w_{Me_2S} = k_3^0 k P_{MeSH} P_{MeOH}^{1/2} P_{H_2O}^{-1} ,$$

$$w_{Me_2O} = k_4^0 k P_{MeOH}^{3/2} P_{H_2O}^{-1} ,$$

$$w_{MeSH} = w_{H_2S} - w_{Me_2S} ,$$

where

$$k = \left(\frac{k_1^0 k_{-5}}{k_{-1}^0 k_5}\right)^{1/2} .$$

When alkali metal ions are introduced into the acid aluminium oxide catalyst, the Lewis acid centres are weakened. This hinders the activation of methanol and methanethiol involved in the formation of dimethyl ether and dimethyl sulfide. As a result, the third and fourth stages (Scheme 7) are suppressed and may be neglected, whereupon the kinetic equation assumes the form

$$w_{MeSH} = \frac{k' P_{H_2S} P_{MeOH}^{1/2}}{[P_{H_2O}(P_{H_2S} + \lambda P_{H_2O})]^{1/2}} ,$$

where

$$k' = \left(\frac{k_1^0 k_2^0 k_{-5}}{k_5}\right)^{1/2} ; \qquad \lambda = k_{-1}^0 k_2^0 .$$

Subject to certain assumptions, this equation is identical with the equation for the kinetics of the conversion of methanol into the thiol on an acid aluminium oxide catalyst. A kinetic equation of the same form has been obtained for the reaction of methanethiol with methanol.[53,81,84,85]

Formally the mechanism of the reversible reaction in which methanethiol decomposes to dimethyl sulfide and hydrogen sulfide is represented by a two-stage scheme:[30,81,85–88] The dissociative chemisorption of methanethiol leads to the formation of hydrogen sulfide and the methoxylation of the surface, after which the methoxide groups interact with a second methanethiol molecule with formation of dimethyl sulfide:

$$CH_3SH + [X_1] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [X_2] + H_2S ,$$

$$CH_3SH + [X_2] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [X_1] + (CH_3)_2S .$$

The simplified kinetic equation for the reaction on an inhomogeneous surface assumes the form

$$w = \frac{k P_{MeSH}^{3/2} (1 - P_{H_2S} P_{Me_2S} / P_{MeSH}^2 K)}{P_{Me_2S}^{1/2}} ,$$

where

$$k = k_1 \left(\frac{k_2}{k_{-2}}\right)^{1/2} .$$

The kinetic equations for the reaction of 1-dodecanol with hydrogen sulfide were derived[56] on the basis of the mechanism:

$$C_{12}H_{25}SH + [X_1] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [X_2] + H_2O ,$$

$$H_2S + [X_2] \xrightarrow{k_2} [X_1] + C_{12}H_{25}SH ,$$

$$C_{12}H_{25}SH + [Y_1] \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Y_2] ,$$

$$[Y_2] \xrightarrow{k_4} [Y_1] + C_{12}H_{24} + H_2S ,$$

$$H_2O + [X_1] \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [X_3] ,$$

where $[X_1]$ and $[Y_1]$ are the active centres on the initial catalyst surface and $[X_2]$, $[Y_2]$, and $[X_3]$ are the active centres on the surface covered by alkoxide groups, the chemisorbed dodecanethiol, and water respectively. The simplified equation

describing the dependence of the rate of formation of dodecane-1-thiol (w_1) and dodecene (w_2) on the partial pressures of 1-dodecanol (P_1), hydrogen sulfide (P_2), dodecane-1-thiol (P_3), and water (P_4) are

$$w_1 = k_1' P_1^{1/2} P_2 P_4^{-1} ,$$

$$w_2 = k_2' P_3 ,$$

where

$$k_1' = k_2 \left(\frac{k_1 k_{-5}}{k_{-1} k_5}\right)^{1/2} ; \quad k_2' = \frac{k_4 k_5}{k_{-5}} .$$

The reaction rates calculated by these equations agree satisfactorily with the experimental values, which confirms the validity of the postulated reaction mechanism.

It follows from the results of a study of the mechanism of the conversion of alcohols into thiols that an active catalyst should ensure in the first place the dissociative chemisorption of the alcohol with formation of reactive alkoxide groups on the surface. This is possible on both acid and basic catalysts. Furthermore, dissociative chemisorption of hydrogen sulfide with formation of thiyl groups reacting with the alkoxide groups should take place on an effective catalyst for the synthesis of an alkanethiol. Such conditions are satisfied by catalysts with paired acid – base centres. In order to reduce the probability of the further reaction of the alkanethiol — its interaction with alkoxy-groups involving the formation of a dialkyl sulfide or decomposition accompanied by the elimination of an alkene, the acid centres must be weakened and the basic centres must be strong. In contrast to the above, an active catalyst for the synthesis of a dialkyl sulfide must contain strong acid centres and moderately strong basic centres. The presence of weakened basic centres promotes the activation of the alkanethiol, which is necessary for its interaction with alkoxide groups and the formation of a dialkyl sulfide, but does not induce the decomposition of the alkanethiol to the alkylthio-groups which readily react further with formation of an alkene.

IV. Selection of catalysts and conditions for the conversion of alcohols into thiols

1. Synthesis of alkanethiols

The results of studies on the synthesis of alkanethiols under various conditions have been published.[3,4,11,14,23,25,29,30,42,48,56] A survey of these data permits the conclusion that, overall, the degree of conversion of the alcohol increases with increase in temperature, contact time, and the hydrogen sulfide : alcohol ratio. Bearing in mind the difficulty of separating an alcohol and an alkanethiol, it is recommended[47] that industrial processes be carried out under the conditions of extensive, best of all total, conversion of the alcohol. With increase in contact time, the yield of the alkanethiol increases only up to a certain value, after which it falls. With increase in temperature, the yield of the alkanethiol also rises, but the selectivity then diminishes. The temperature for conversion of higher alcohols into thiols is lower than for methanol. An increase in selectivity with respect to the alkanethiol is promoted by an increase in the hydrogen sulfide : alcohol ratio, especially in the conversion of higher alcohols into thiols. However, even in the presence of a large excess of hydrogen sulfide in the system, the selectivity with respect to the formation of alkane-2-thiols is low. It rises when carbonyl compounds are added to the reaction mixture. Thus the addition of 5 mass% of acetone to 2-propanol on a 4% K_2O/Al_2O_3 catalyst increases the overall rate of reaction by a factor of 4, while the selectivity with respect to propane-2-thiol increases from 50% to 80%. A much smaller effect is observed in the case of primary alcohols.[40]

The rate of formation of the alkanethiol increases in proportion to the partial pressure of hydrogen sulfide and the partial pressure of the alcohol (in the conversion of 1-propanol into the thiol)[5] or its square root (in the conversion of methanol and 1-dodecanol into the thiols).[56] In practice, the thiols are synthesised in the following ranges of parameters: synthesis temperatures of 350–420 °C for methanethiol and 300–350 °C for its homologues; contact time 5–35 s depending on the temperature; molar ratio hydrogen sulfide: alcohol = 1.5–7.5; overall pressure in the system as a rule not above 1 MPa.[47]

Table 7. Optimum conditions in the synthesis of alkanethiols on basic catalysts at $P = 0.1$ MPa.

Alcohol	Catalyst	Reaction conditions			Degree of conversion of alcohol (%)	Yield of alkanethiol (%)	Ref.
		T/°C	M	τ/s			
Methanol	10% K_2WO_4/Al_2O_3	400	2	5.6	92.7	90.9	4
	10% K_2WO_4/Al_2O_3	320	1.8	39[a]	98.5	90	89, 90
	K_2WO_4/Al_2O_3	400	1.5	10.5[b]	100	80	47
	25% K_2WO_4/SiO_2	360	1.6	25	84	77	31
	20% K_2CO_3/SiO_2	360	1.6	25	84	75	31
	2.9% Na_2O/Al_2O_3	360	1.6	4.2	80	75	31
	6.4% K_2CO_3/AlO	360	1.6	8.4	74	72	31
	10% K_2WO_4/Al_2O_3	360	1.6	4.2	95	62	31
Ethanol	10% K_2WO_4/Al_2O_3	318	2.86	5.6	83.4	68.7	2, 4
1-Propanol	K_2WO_4/Al_2O_3	330	3	10	95	80	47
1-Butanol	4.3% K_2O/Al_2O_3	300	10	10.4	93	91	15
2-Butanol	K_2WO_4/Al_2O_3	275	4	0.9[b]	59	15	47
	K_2WO_4/Al_2O_3	300	4	0.3	71	8	47
1-Hexanol	K_2WO_4/Al_2O_3	310	7.5	10.7[c]	100	80	47
1-Octanol	10% K_2WO_4/Al_2O_3	287	7.73	7.4	100	91	2, 4
1-Dodecanol	K/Al_2O_3	300	15	2.5	100	70	46, 92

[a] $P = 0.8$ MPa; [b] $P = 0.3$ MPa; [c] $P = 0.2$ MPa.

High yields of alkanethiols may be obtained under certain conditions on a series of supported acid catalysts and on zeolites in the cationic form. However, the process is insufficiently selective, particularly in the syntheses of methanethiol homologues and the selectivity of the above catalysts cannot be increased by varying the reaction conditions. Supported basic catalysts, in particular alkali-modified Al_2O_3, exhibit a high selectivity with respect to alkanethiols: in their presence, the selectivity is close to 100%. Table 7 presents the optimum conditions for the syntheses of alkanethiols on such catalysts.

The quality of the alkaline aluminium oxide catalyst for the synthesis of alkanethiols is influenced not only by the nature of the active component but also by its content on the surface, as well as by the characteristics of the carrier — specific surface, porous structure, phase composition, and purity. Although the use of various alkaline additives is usually mentioned, in practice potassium tungstate deposited on Al_2O_3 is apparently employed, its content being $\geqslant 10$ mass%.[3,4,89–91] The active component must be present on the surface in a highly disperse state, so that the Al_2O_3 used as the carrier must have a specific surface not less than 200 $m^2\ g^{-1}$.[89–91] The presence of an considerable number of transport pores in the catalyst is necessary in order to rule out diffusional complications. γ-Al_2O_3 is usually employed, but the use of other phases is also permissible.[93] The method used to prepare the catalyst is also important, but the relevant data have scarcely been published or it has been stated[2–4] that the catalyst was prepared by impregnation or mixing methods.

The active and selective IKT-31-1 catalyst for the synthesis of methanethiol from methanol and hydrogen sulfide has been developed by the Institute of Catalysis of the Siberian Division of the Russian Academy of Sciences jointly with the Special Technical Design Bureau for Catalysts. It is prepared in two ways.[93] In the first procedure, an aqueous solution of the alkali metal compound is deposited in the form of an aerosol on an aluminium oxide carrier incorporating γ-Al_2O_3 and 20%–30% of χ-Al_2O_3 with a large macropore volume (radius exceeding 100 nm). The second procedure consists in mixing an aqueous solution of the active substance with aluminium hydroxide and subsequent granulation. The specimens obtained are heat-treated. The IKT-31-1 catalyst is employed in the industrial manufacture of methionine (the stage involving the synthesis of methanethiol) by the 'Orgsintez' Volga Industrial Conglomerate.

Alkaline aluminium oxide catalysts are more stable in the reaction involving the conversion of alcohols into thiols than the unpromoted Al_2O_3.[3,4] The activity of the catalyst does not change when the starting material contains carbon disulfide or dimethylamine[4] and also carbon monoxide[47] as impurities. Although water in fact inhibits the process, its presence in an amount of 0.5 mass%–1 mass% has a positive effect on the stability of the catalyst.[3,4] Preliminary sulfiding of the catalyst by treatment with hydrogen sulfide before use has a stabilising effect on it.[5,91] The stability of the catalyst is reduced if the process is carried out at a temperature exceeding 420 °C, since the surface becomes saturated with coke.[3] For the stable operation of the alumino–potassium tungstate catalyst, it is important to provide for the effective removal of heat from the system. The simultaneous passage of methanol and hydrogen sulfide through the K_2WO_4/Al_2O_3 catalyst at an initial temperature of 320 °C leads to the heating of the catalyst, which decreases its surface area and the yield of methanethiol. This deficiency is eliminated by dividing the catalyst into consecutively arranged layers, all the hydrogen sulfide being introduced into the first layer, whilst methanol is added in portions to each catalyst layer. This ensures the stable operation of the catalyst for three years.[89–91]

2. Synthesis of dialkyl sulfides

It has been stated in patent specifications (see the relevant reviews[2,8]) that various dialkyl sulfides R_2S ($R = C_1 - C_{12}$) may be obtained under certain conditions by the reactions of alcohols with hydrogen sulfide, but real results have been published only for the synthesis of dimethyl sulfide.

The parameters of the synthesis of dimethyl sulfide are influenced by the reaction conditions. Thus an increase in the yield of dimethyl sulfide is promoted by an increase in temperature and contact time and by a decrease in the hydrogen sulfide : alcohol ratio.[2,11,12,14,17,23,25,28,30,94] The rate of formation of dimethyl sulfide increases with increase in the partial pressure of methanol and of the methanethiol formed from it. On acid aluminium oxide catalysts, the rate of reaction increases with the square root of the partial pressure of methanol and with the partial pressure of methanethiol; water inhibits the process.[49,79,81]

It follows from the analysis of the kinetic equations obtained that, in order to increase the selectivity with respect to dimethyl sulfide, it is necessary to carry out the process at a reduced partial pressure of methanol, while the hydrogen sulfide concentration should be below that required for the establishment of the stoichiometric component ratio (0.5 : 1).

In the presence of alkaline catalysts, high yields of dimethyl sulfide cannot be attained by varying the conditions in the reactions of methanol with hydrogen sulfide. This can be achieved only by employing acid catalysts and also cationic forms of zeolites on the surfaces of which strong Brønsted acid centres arise under the reaction conditions. Table 8 indicates the optimum conditions for the synthesis of dialkyl sulfides on acid catalysts. Evidently dimethyl sulfide may be obtained in an almost quantitative yield (up to 97 mol%). However, the synthesis of its homologues is difficult. Thus a relatively high yield of diethyl sulfide (up to 67 mol%) is reached in the reaction of ethanol with hydrogen sulfide only on cationic forms of zeolites. On other catalysts, active in the synthesis of dimethyl sulfide, dialkyl sulfides are not formed in the interaction of higher alcohols with hydrogen sulfide even when the reaction conditions are varied.

The achievement of the second stage in the reaction of an alcohol with hydrogen sulfide, namely its interaction with the alkanethiol, gives rise to considerable possibilities for the synthesis of dialkyl sulfides from higher alcohols in a preparative yield.

The interaction of methanol with methanethiol has been investigated[9,10,53,75,95] in the presence of various acid catalysts (see, for example, Table 6). The reaction conditions influence the rate and mode of this process.[53,81,84,85] With increase in temperature, the degree of conversion of the reactants and the yield of dimethyl sulfide also increase. At a constant temperature, the degree of conversion of the reactants and the yield of dimethyl sulfide increase with contact time; dimethyl ether is formed as a side product, its yield diminishing with increasing degree of conversion of the alcohol. Dimethyl ether and dimethyl sulfide are formed via independent paths. The rate of formation of dimethyl sulfide increases in proportion to the square root of the partial pressure of methanol and to the partial pressure of methanethiol, water inhibiting the process. An equation taking into account the degree of utilisation of the catalyst surface when the reaction takes place under conditions of internal diffusion has been obtained.[96] It follows from the analysis of the kinetic data that the influence of the side reaction involving the formation of dimethyl ether diminishes, while the selectivity with respect to dimethyl sulfide increases with decrease in the methanol : methanethiol ratio and with increase in the degree of conversion of methanol.

Unfortunately, only isolated examples of the synthesis of higher dialkyl sulfides by this procedure have been described. Thus the interaction of ethanethiol with aliphatic $C_1 - C_4$ alcohols on Al_2O_3 and AlSi results in the formation of alkyl ethyl sulfides.[95]

Table 8. Optimum conditions for the synthesis of dialkyl sulfides by the reactions of alcohols with hydrogen sulfide on catalysts having different compositions.

Alcohol	Catalyst	Reaction conditions			Degree of conversion of alcohol (%)	Yield of dialkyl sulfide (mol%)	Ref.
		T/°C	M	τ/s			
Methanol	WO_3	360	1.6	4.2	99	34	11
	TiO_2	350	2	~5	91	37	14
	γ-Al_2O_3	300	0.5	12	100	94	94
	γ-Al_2O_3	350	1.0	~6	99	83	14
	γ-Al_2O_3	450	0.6	7.5	100	94	23
	η-Al_2O_3	400	0.6	0.84	100	96	16
	HPW	360	1.6	1.2	80	64	30
	AlSi	360	1.6	6.3	87	54	11
	HNaY	300	1.0	~6.5	98	92	25, 26
	HZSM-5	350	1.0	~4.5	98	93	25, 26
	HZSM-5	400	0.6	1.2	100	88	29
	NaX	350	0.5	~6	65	40	25, 26
	25% $HSiW/SiO_2$	360	1.6	1.1	100	80	30
	7% WO_3/SiO_2	360	0.6	4.2	80	59	11
	2.3% Cr_2O_3/SiO_2	360	0.6	3.7	85	52	12
	15% MoO_3/SiO_2	360	1.6	4.2	92	42	12
	0.3% Cr_2O_3/Al_2O_3	400	0.6	7.5	100	96.8	23
	0.3% CuO/Al_2O_3	400	0.6	7.5	100	90	23
	7% WO_3/Al_2O_3	360	0.6	1.1	80	56	12
	10% V_2O_5/Al_2O_3	360	0.6	0.6	80	32	12
Ethanol	WS_2	280	3.3	4	99	27	2
	TiO_2	320	2.5	3.1	97	9	2
	γ-Al_2O_3	317	2.86	5.6	93	1.6	3
	NaX	350	2	~6	–	5	24
	CdNaX	250	2	~6	85	67	36, 37
	ZnNaX	250	2	~6	76	60	36, 37
	CoNaX	250	2	~6	73	54	36, 37
	NiNaX	300	2	~6	76	25	37
1-Propanol	CdNaX	350	4	~6	80	< 10	36
1-Dodecanol	K/Al_2O_3	300	15	2.5	100	~6	46, 56, 92

V. Conclusion

Thus the studies initiated previously on the gas-phase heterogeneous-catalytic synthesis of alkanethiols and dialkyl sulfides from alcohols and hydrogen sulfide have developed further in our time. During the last 20–25 years, the main efforts in this field have been directed to the determination of the relation between the catalytic and acid–base properties of catalysts of various composition and to the elucidation of the mechanism of the thiolation reactions by means of a set of physicochemical methods (kinetic, adsorption, IR spectroscopic, and NMR methods). This made it possible to create active and selective catalysts for the synthesis of methanethiol and dimethyl sulfide, which are widely used in the manufacture of methionine (a food additive) and dimethyl sulfoxide (extractant, solvent, medicinal preparation). Higher alkanethiols (C_2–C_{12}) can be obtained in fairly satisfactory yields by the interaction of hydrogen sulfide with 1- and 2-alkanols on the catalysts proposed. The alkanethiols are employed as odorants for fuel gases, as starting materials for the synthesis of agrochemicals, as domestic chemicals, as surfactants, and as regulators of the polymerisation processes in the manufacture of raw rubbers and plastics.[97] The parameters of the processes involving the synthesis of higher alkanethiols which have been achieved may be improved by a more precise regulation of the acid–base characteristics of the catalyst surfaces.

The problem of the creation of effective catalysts for the synthesis of dimethyl sulfide homologues is still by no means fully solved. Active catalytic systems have been found only for the synthesis of diethyl sulfide. It has so far been impossible to obtain dialkyl sulfides in preparative yield by the interaction of higher alcohols with hydrogen sulfide, because the thiolation process is complicated by the occurrence of competing reactions. There are good prospects for the practical utilisation of dialkyl sulfides, since they can serve as extractants for noble metals, as flotation agents, and as additives to oils. They can also be used as the starting compounds for the synthesis of biologically active substances.[97] Bearing in mind the practical importance of dialkyl sulfides and the availability of the starting material, it may be expected that studies in the field of their catalytic synthesis will be continued, primarily with the aim of elucidating the detailed reaction mechanism, since this will help in the deliberate regulation of the properties of the catalyst and in controlling the thiolation process.

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