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Catalytic reactions of dialkyl disulfides

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The results of studies into catalytic transformations of lower dialkyl disulfides (Alk = C_1-C_4) are summarized and described systematically. The decomposition, cyclization, hydrogenolysis, oxidation and thioalkylation reactions are considered. The results of reactions are compared depending on the catalyst nature and reaction conditions.
The bibliography includes 181 references.

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I. Introduction

Organic disulfides are highly reactive and, therefore, they are used to synthesize various sulfur compounds many of which are promising for practical applications (see, for example, a monograph [1]). Methanetiol can be used for the synthesis of methyonin (a drug and a nutrition additive for livestock and poultry), alkanethiols RSH (R = C_2-C_4) serve as odorants for fuel gases and as starting compounds for preparing agrochemicals, household chemicals and surfactants. Dialkyl sulfides are used as floatation reagents, odorants and as starting compounds for the preparation of practically valuable substances. For example, dimethyl sulfide is used to prepare dimethyl sulfoxide — a medication, a solvent and an extractant for noble and rare metals. Thiophene serves for the synthesis of polymers, physiologically active compounds, dyes, oil additives and polyorganylsiloxanes. Alkanethiosulfinates and -sulfonates are antibactericidal and anti-inflammatory agents; alkanesulfonic acids are efficient acid catalysts for some reactions and starting reactants for the synthesis of medications. (Alkylthio)thiophenes improve characteristics of lubricating oils and polymers by increasing their stability against thermal oxidation; (alkylthio)phenols are antioxidants, they can be used in the production of herbicides, pesticides and pharmaceutical agents.

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Dialkyl disulfides required to prepare the above products are synthesized by known procedures but in amounts insufficient for broad practical use. There are non-catalytic methods for the synthesis of various compounds based on dialkyl disulfides. However, most of them consist of many steps and require the use of expensive and difficult-to-obtain substances, the processes are very slow and complicated for implementation. As in many other cases, more promising are catalytic methods that enable more advantageous chemical processes and more efficient process flow diagrams. The development of catalytic syntheses using lower dialkyl disulfides has been held up until recently due to the absence of accessible and cheap disulfide raw material. Currently, the amount of sulfur-containing hydrocarbon mixtures (natural, associated petroleum and waste gases, crude oil and oil products) being processed has markedly increased and the capacity of these plants steadily grows. Since the production, processing, application, transportation and storage of sulfur-containing hydrocarbon mixtures bring about a number of environmental and technological problems, these products are treated to remove sulfur. For purification of sulfur-containing products from thiols, oxidative methods are widely used,[2] which produce huge amounts of mixtures of lower dialkyl disulfides R_2S_2 with R = C_1-C_4 (dialkyl disulfides with R = C_1-C_2 predominate). The disposal of these products is a challenging task. Their combustion gives off sulfur dioxide, carbonyl compounds and other products polluting the environment. Attempts are made to utilize non-destroyed dialkyl disulfides. For example, dimethyl disulfide recovered from the mixture is proposed as an odorant for natural gas, a coking inhibitor for the pyrolysis of hydrocarbon raw materials, for agrochemistry and for sulfiding hydrotreating catalysts.[3] Lower dialkyl disulfides can be used as readily accessible and inexpensive raw

materials for the synthesis of valuable organic compounds of sulfur.

The chemistry of organic disulfides has been studied rather comprehensively (see, for example, reviews[4,5]). The development of new catalytic syntheses using lower dialkyl disulfides requires detailed investigations. The complexation and adsorption of dialkyl disulfides on various catalysts have been studied to date at a modern level using the most advanced physicochemical methods, and the mechanisms of these processes preceding the catalytic step have been elucidated, which is important for the understanding of known reactions and prediction of new reactions. In the field of catalysis of reactions involving lower dialkyl disulfides, a large body of information has also been accumulated to date but no survey publications are available. A monograph[4] and a review[5] are devoted to the chemistry of organic sulfur compounds. These studies and one more monograph[6] dealing with heterogeneous catalysis of organic sulfur compounds even do not mention the reactions of dialkyl disulfides, while the monograph by Mashkina[1] considers only the syntheses of thiols by catalytic transformations of dimethyl and diethyl disulfides.

The present review describes systematically and analyzes the existing published data on the catalysis of reactions involving lower dialkyl disulfides R_2S_2 with $R = C_1-C_4$ published before 2013 and, since this is the first review, it also includes earlier papers. The reactions proceeding under inert atmosphere, hydrogenolysis with molecular hydrogen, oxidation and thioalkylation of alcohols and unsaturated and aromatic compounds are considered.

II. The properties of lower dialkyl disulfides

For elucidation of the possibility of reactions of lower dialkyl disulfides and discussion of reaction mechanisms, it is necessary to take into account the properties of these compounds, in particular, the electronic structure, bond strength, reactivity towards various compounds in solutions, complexation, adsorption, thermal decomposition, *etc*. Therefore, below we outline the known data on the properties of lower dialkyl disulfides important for the understanding of their catalytic transformations.

1. Physicochemical properties

The physicochemical properties of dialkyl disulfides have been considered in detail in reviews.[4,5] Dialkyl disulfides have C–H, C–S and S–S bonds. The planes bearing the alkyl groups are perpendicular to each other. The sulfur atoms in dialkyl disulfides have lone electron pairs and can participate in reactions as electron donors. The strong interaction of the lone electrons of sulfur accounts for the partial π-character of the S–S bond, which decreases the electron-donating properties of sulfur atoms as compared, for example, with dialkyl sulfides. The conjugation with the 3d orbitals of the dithio group facilitates the proton elimination from the methylene group adjacent to the S–S group. The S–S bond is less strong than C–S or C–H bonds. Since the configuration of the C–S–S–C polar core of various di-n-alkyl disulfides is approximately the same, the bond strength does not depend much on the length of the alkyl chains. In dialkyl disulfides with branched alkyl groups, the C–S bond is weaker than the S–S bond.

The S–S bond can be cleaved under the action of nucleophilic and electrophilic agents. Presumably, the primary attack in these reactions is directed on one of the disulfide sulfur atoms. This results first in polarization of the S–S bond and then this bond is cleaved. In the presence of Brönsted acids, the reaction proceeds *via* electrophilic addition of a proton to the disulfide followed by cleavage to give the sulfenium ion; this ion decomposes to thioaldehyde, which is readily polymerized (Scheme 1).

Scheme 1

$$CH_3SSCH_3 \xrightarrow{[H^+]} \left[CH_3\overset{+}{S}SCH_3\right] \xrightarrow[-CH_3SH]{} CH_3S^+ \longrightarrow$$
$$\longrightarrow CH_2{=}S \longrightarrow (CH_2S)_n$$

Under the action of nucleophilic agents, for example, alkalis, the reaction also starts with the attack on the sulfur atom followed by S–S bond cleavage. The S–S bond in disulfides is also broken on treatment with free radicals or on exposure to UV radiation, this gives radicals that undergo further transformations.

2. Thermal decomposition of dialkyl disulfides

On heating to high temperature, dialkyl disulfides decompose. Dimethyl disulfide[5,7–9] kept at 316–373 °C in a steady-state reactor for 3–120 min decomposes after an induction period, which is 0.3–11.5 min depending on the experimental conditions. The reaction products contain methanethiol (39%), hydrogen sulfide (28%), ethylene (16.6%), carbon disulfide (10%), traces of thiophene and alkyl polysulfides (5.5%). The reaction is assumed to follow a radical mechanism. In the initial step, dimethyl disulfide cleaves at the S–S bond to give the $CH_3S^{\bullet}$ radicals. They react with disulfide to give methanethiol and the $CH_3SSC^{\bullet}H_2$ radical, which decomposes yielding thioformaldehyde and the $CH_3S^{\bullet}$ radical (Scheme 2).

Scheme 2

$$CH_3SSCH_3 \longrightarrow 2\,CH_3S^{\bullet}$$
$$CH_3S^{\bullet} + CH_3SSCH_3 \longrightarrow CH_3SH + CH_3S\dot{C}H_2 \longrightarrow$$
$$\longrightarrow CH_2{=}S + CH_3S^{\bullet}$$

Thioformaldehyde is an unstable compound, which is converted to the corresponding polymer $(CH_2S)_n$ or reacts with dimethyl disulfide to afford alkyl polysulfides $CH_3S_nCH_3$. However, the opinion that the pyrolysis of dimethyl disulfide in toluene at 462–560 °C follows a molecular mechanism was also stated.[9] Details of the mechanism of pyrolysis of dimethyl disulfide are discussed in some other papers, both experimental and theoretical.[10–12] In disulfides with branched carbon chains, the C–S bond is weaker than the S–S bond. Pyrolysis of these dialkyl disulfides occurs by a molecular mechanism.[13] Decomposition of diisopropyl disulfide at 500 °C involves the intermediate formation of isopropylsulfane and results in the formation of propylene and hydrogen sulfide. The gas-phase thermolysis of di-*tert*-butyl disulfide at 330–440 °C affords 2-methylpropylene and disulfane, the decomposition of the latter resulting in hydrogen sulfide and sulfur.[14]

Upon thermolysis of dialkyl disulfides, the formation of thiophene is possible. Indeed, diethyl disulfide decomposes at 496 °C by 73% to release thiophene, hydrogen sulfide, diethyl sulfide, ethanethiol, free sulfur, saturated and unsaturated hydrocarbons and resins.[15] According to a number of studies,[16–18] diethyl and dibutyl disulfides decompose at 400–650 °C to give thiophene (5 mol.%–11 mol.%),

hydrocarbons and hydrogen sulfide (at lower temperature, thiophene is not detected among the reaction products). Pyrolysis of dialkyl disulfides in a flow-type quartz reactor at 580–610 °C in a nitrogen atmosphere results in their complete decomposition.[19] Dimethyl disulfide decomposes to give mainly carbon disulfide (23.5% yield) and thiophene (0.12%). In the pyrolysis of diethyl disulfide, the yield of thiophene increases to 6%, while the yield of carbon disulfide decreases down to 9.5%. Thermolysis of a mixture of dialkyl disulfides (dimethyl, methyl ethyl and diethyl disulfides) gives rise to thiophene (5.5% yield), carbon disulfide (19.2%) and thienothiophene (0.3%).

3. Complex formation and adsorption of dialkyl disulfides

In the beginning of a catalytic reaction, dialkyl disulfide interacts with the catalyst active sites; therefore, below we briefly consider the available data on this interaction.

Dialkyl disulfides in solutions form complexes with chloroform,[20] Ca, Zn, Cd, Pb and Ag nitrates and perchlorates,[21] cobalt carbonyl,[22,23] Al, B, Ga and Sn halides[24] and Ni, Ru and Pd complexes.[25–27] In all cases, 1 : 1 complexes are formed with the participation of a disulfide sulfur atom, only one sulfur atom being involved in the donor–acceptor bond. The complex formation results in activation of the dialkyl disulfide molecule. In some cases, for example under the action of mercury chloride or acetate,[28] cobalt or nickel carbonyls [22,25] or copper compounds,[21] the complexation is accompanied by S–S bond cleavage.

The adsorption of lower dialkyl disulfides on some single-crystal faces, metal films and solid catalysts has been studied in detail using various physicochemical methods (temperature-programmed desorption, X-ray photoelectron spectroscopy, IR spectroscopy, low-energy electron diffraction, extended X-ray absorption fine structure (EXAFS) analysis, tracer method, *etc.*) and theoretical calculations.

The adsorption of dimethyl and diethyl disulfides was studied in most detail on single crystals and films. Upon the adsorption of dimethyl disulfide on Cu(111)[29–32] at −195 °C, surface CH_3S structures appear, while at −53 °C some CH_3S groups decompose to give surface methyl groups, which undergo various transformations when heated to >150 °C (Scheme 3). In addition, sulfur and carbon are deposited on the surface. Diethyl disulfide is adsorbed on the Cu(111) face similarly to dimethyl disulfide.[31] The formation of the ethylthio group from diethyl disulfide starts at −193 °C and ends at −70 °C. At 107–127 °C, ethane and ethylene are evolved in a ratio depending on the surface coverage by thiolate groups.

Scheme 3

$$CH_3S\,(ads) \longrightarrow S\,(ads) + CH_3\,(ads)$$

$$CH_3\,(ads) + H\,(ads) \longrightarrow CH_4\,(gas)$$

$$2\,CH_3\,(ads) \longrightarrow C_2H_6\,(gas)$$

$$2\,CH_3\,(ads) \longrightarrow C_2H_4\,(gas) + 2\,H\,(gas)$$

$$CH_3\,(ads) \longrightarrow C\,(ads) + 3\,H\,(ads)$$

$$2\,H\,(ads) \longrightarrow H_2\,(gas)$$

ads means adsorbed, gas means gaseous

The adsorption of disulfides on the Au(111) surface has been studied in detail.[33–36] The diethyl disulfide chemisorption on Au(111) at low surface coverage affords only ethylthiolate groups; as the coverage increases, they are converted to give S–Au structures. The chemisorption of dimethyl and di-n-butyl disulfides on Au(111) at 27 °C is accompanied by the formation of MeS and Bu^nS structures. In the case where dibutyl disulfide is adsorbed on a surface pre-saturated with MeS structures, the MeS and Bu^nS groups react to give methyl n-butyl disulfide. At temperatures of >127 °C, extensive decomposition of di-n-dibutyl disulfide takes place with evolution of sulfur and hydrocarbons. In ethanol, dimethyl disulfide is adsorbed on the Au(111) face[37] at room temperature to give a methylthiolate monolayer, which is formed during 1 min. As the residence time of the disulfide in solution increases, the S–C bond in the MeS structures is cleaved to give atomic sulfur, polysulfide and carbon species on the surface. Some of the MeS structures are oxidized to thio-oxymethylene (SCH_2O), which decomposes to give atomic sulfur (which remains adsorbed on the surface) and formaldehyde.

Chemisorption of dimethyl disulfide on the Mo(110) face[38] at −23 °C is accompanied by S–S bond cleavage yielding the MeS structures. Above 27 °C, thiolate structures decompose at the C–S bond yielding CH_3 groups, which react with the surface OH groups to give methane and hydrogen; in addition, carbon and sulfur are deposited on the surface. Diethyl disulfide is dissociatively chemisorbed on the Ge(110) surface to produce germanium-bonded EtS structures.[39] The S–S bond remains unchanged upon the adsorption of dimethyl disulfide on the Si(100) surface at room temperature and only after heating to 440 °C, this bond is cleaved to give surface CH_3S groups.[40] On the Ni(111) face, dimethyl disulfide is adsorbed with dissociation of the S–S bond; some molecules decompose at a temperature of −123 °C, while other molecules decompose at −23 °C. This yields surface methylthio groups. As the temperature rises to −3 °C, they further decompose to give methane, ethylene, ethane and hydrogen; this process ends at 200 °C.[41] The chemisorption of dimethyl disulfide on GaAs(100)[42,43] involves both Ga and As atoms. The resulting thiolate structures on the Ga atoms react with the surface hydrogen and at 77–112 °C, they are desorbed as molecular methanethiol. The thiolate groups on As atoms are more stable but at 247 °C, they decompose with C–S bond cleavage. The chemisorption of diethyl and dibutyl disulfides on GaAs(100) gives rise to surface C_2H_5 and C_4H_9 groups, which then decompose to give ethylene, butylene and surface sulfur. Dimethyl disulfide is chemisorbed on the zinc oxide surface.[44,45] At 27 °C, only associative adsorption takes place on ZnO(0001), while on ZnO(000$\bar{1}$), dimethyl disulfide is chemisorbed with S–S bond cleavage to form MeS structures, which cover the surface to a less than a monolayer. The methylthio groups react with the surface hydroxyl groups to give methanethiol. At higher temperature, the methylthio groups that have formed decompose along different pathways. The coupling of neighbouring methylthio groups results in the formation of dimethyl sulfide and evolution of sulfur; methyl groups migrate to surface oxygen atoms and, at 250 °C, they are dehydrogenated and oxidized to CH_2O, which can decompose at 287 °C with evolution of carbon oxides and, possibly, also sulfur dioxide. The presumed reactions are shown in Scheme 4.

Scheme 4

$$CH_3S\ (ads) + OH\ (ads) \longrightarrow CH_3SH\ (ads) + O\ (latt)$$

$$2\,CH_3S\ (ads) \longrightarrow (CH_3)_2S\ (gas) + S\ (ads)$$

$$CH_3S\ (ads) + O\ (latt) \longrightarrow CH_2O + S\ (gas) + OH\ (ads)$$

O (latt) is an oxygen atom of the oxide lattice

At 27 °C on the ZnO(0001) surface, diethyl disulfide is dissociatively chemisorbed on cationic and anionic sites, which is accompanied by S–S bond cleavage to give EtS structures on the surface; at 187 °C, they are converted to give ethylene and adsorbed sulfur. Only associative adsorption occurs on ZnO(000$\bar{1}$).[46] Thus, the adsorption of dialkyl disulfides on various metal films and single crystals is accompanied by decomposition at the S–S bond to give AlkS structures even at low temperature. As the temperature rises, these structures undergo various transformations to yield alkanethiols, dialkyl sulfides, hydrocarbons, sulfur and, in some cases, oxygenated compounds.

The dialkyl disulfide adsorption on some solid catalysts was investigated. The dissociative chemisorption of disulfides was found to be the major process in this case. On the 20% Ni/SiO_2 catalyst at 27 °C, dimethyl and di-n-butyl disulfides are dissociatively chemisorbed[47] with S–S bond cleavage. The resulting AlkS structures further decompose at the C–S, C–H and C–C bonds to give a variety of compounds. The methylthio groups are converted to methanethiol, dimethyl sulfide, methane, hydrogen and carbon monoxide; butylthio groups give n-butanethiol, di-n-butyl sulfide, butylene, thiophane, hydrogen, methane, ethane and carbon monoxide. At a temperature of >327 °C, carbon and a large amount of sulfur are formed. The dissociative adsorption and the reactions occur only on the nickel surface rather than on the support. On pure silica,[48] dimethyl disulfide is associatively adsorbed at 20 °C to form a hydrogen bond between the disulfide sulfur atom and the OH groups of SiO_2. This is manifested in the IR spectra as a decrease in the intensity of the OH stretching band and the shift of this band from 3750 to 3535 cm^{-1}. The interaction of dimethyl disulfide with HY zeolite (Si : Al = 20) at atmospheric pressure and 50 °C gives rise to bonds between the lone electron pair of disulfide sulfur and the zeolite proton. After desorption at 100 °C, the hydroxyl groups of the surface are completely restored. At higher temperature, the disulfide S–S bond is cleaved to give CH_3S groups and methanethiol.[49] On contact with γ-Al_2O_3, dimethyl disulfide forms a hydrogen bond with the surface hydroxyl groups, which is manifested in the IR spectrum as the shift of the OH stretching band from 3750 to 3630 cm^{-1}. The hydrogen bond breaks upon evacuation of the sample. In addition, the IR spectrum exhibits the stretching and bending absorption bands for the methyl and methylene groups, which disappear after heating of the sample to 300 °C. Surface reactions giving sulfonate, sulfate, thiocarboxylate, thiocarbonate and carbonate-carboxylate surface groups occur upon dimethyl disulfide adsorption to a minor extent. These products have high thermal stability and can be completely removed from the surface only at 400–500 °C.[50] The adsorption of dimethyl disulfide on V_2O_5/Al_2O_3 at 185 °C is accompanied by S–S bond cleavage to give MeS structures, which react with the surface oxygen atoms yielding sulfonate groups. At higher temperature, they are converted to sulfate structures and sulfur dioxide. These surface structures are stable up to 300 °C but at 400 °C, they are completely removed from the surface.[51] On the MnO_2 catalyst [52] having active oxygen atoms on the surface, similar processes take place but dissociation with S–S bond cleavage already occurs at 20 °C.

III. Catalytic transformations of dialkyl disulfides under inert atmosphere

Under inert atmosphere and under the action of solid catalysts, dialkyl disulfides decompose at elevated temperature to give various products.

1. The formation of alkanethiols and dialkyl sulfides

In the presence of bulk and supported catalysts, dimethyl and diethyl disulfides decompose to yield alkanethiols, dialkyl sulfides, hydrogen sulfide, carbon disulfide, sulfur, C_1–C_2 hydrocarbons, resins and coke.[53–56] Upon dimethyl disulfide decomposition on some catalysts, dimethyl sulfide and methanethiol are formed in comparable amounts, while on some other catalysts one of these products predominates. In the presence of catalysts of various compositions at a constant temperature, increase in the contact time (τ/s) entails an increase in the degree of conversion of dimethyl disulfide [*X* (%)]. The selectivity [*S* (%)] of formation of all products upon decomposition below 200 °C does not change with an increase in the conversion, *i.e.*, the products are formed from the disulfide along independent pathways. At higher temperature, an increase in the degree of conversion of dimethyl disulfide leads to a decrease in the selectivity with respect to methanethiol and an increase with respect to dimethyl sulfide and hydrogen sulfide due to condensation of the resulting methanethiol (Fig. 1).[55,57] In the case of transformation of diethyl disulfide on pure γ-Al_2O_3 and on γ-Al_2O_3-supported B, Na, Mo and Co

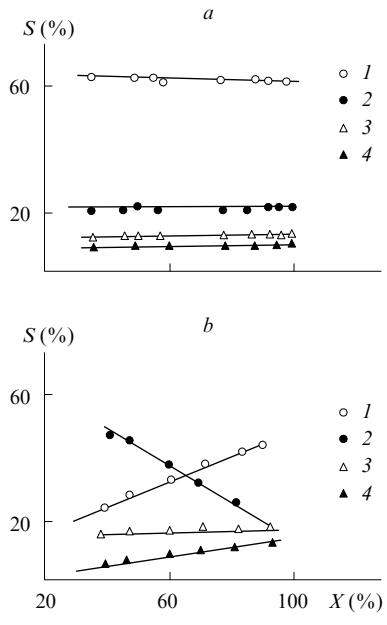
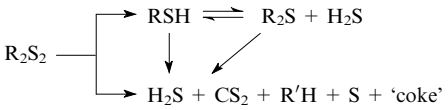


Figure 1. Selectivity of formation of dimethyl sulfide (*1*), methanethiol (*2*), H_2S (*3*), CS_2 (*4*) at different degrees of conversion of dimethyl disulfide catalyzed by 10% Co/Al_2O_3 at a temperature of 150 (*a*) and 320°C (*b*).[56]

oxides and K_2WO_4 (see Ref. 57), ethanethiol predominates among the organosulfur compounds, the yield of diethyl sulfide is decreased; substantial amounts of ethylene and hydrogen sulfide are formed, resulting from both the starting diethyl disulfide and the produced ethanethiol and diethyl sulfide. These reactions easily proceed in the presence of other catalysts,[58] which reduces the selectivity of formation of organic sulfur compounds. The selectivity of formation of all products upon disulfide decomposition below 200 °C does not change with an increase in the conversion, while at higher temperature, the selectivity to thiol decreases and that to disulfide and hydrogen sulfide increases due to thiol condensation. In the general case, the dialkyl disulfide transformation under inert atmosphere occurs by a parallel-successive chart (Scheme 5).

Scheme 5



R = Me, Et; R′H is methane, ethylene

The maximum selectivity to alkanethiol at 250–350 °C is 60%–70% in the decomposition of dimethyl disulfide and 30%–60% for diethyl disulfide.

In the transformation of dimethyl and diethyl disulfides, the oxide catalysts differ in the activity characterized by the rate (w) of disulfide decomposition at a constant conversion and by the selectivity of formation of the reaction products (Table 1). In order to find out which surface active sites perform the reactions yielding dimethyl sulfide and methanethiol from dimethyl disulfide, catalysts differing by the type, strength and concentration of acidic and basic sites on their surface were compared.[55] The acid-base properties of these catalysts were studied by IR spectroscopy based on the adsorption of probe molecules.[59] The strength of the sites (in kJ mol^{-1}) was determined as follows: from the CO adsorption heat (Q_{CO}) for the Lewis acid sites (LAS); from the affinity of $CDCl_3$ deuterium for the sites (PA^o) for the basic sites (BS); and from the proton affinity for pyridine (PA^c) for the Bröonsted acid sites (BAS). The acid-base properties of some catalysts are summarized in Table 2.

Table 1. Transformation rate of dimethyl disulfide (w) and selectivity of product formation in the reaction of dimethyl disulfide on oxide catalysts in an inert atmosphere (250 °C, the conversion of dimethyl disulfide is 60%).[55, 56]

Catalyst	w [a]	Selectivity (%)			
		$(CH_3)_2S$	CH_3SH	H_2S	CS_2
K_2WO_4/SiO_2	2.8	3.2	68	10	12
NaX	3.7	6.0	50	10	24
$HSiW/SiO_2$ (see [b])	0.18	28	31	20	17
HZSM-5	21.9	36	42	18	6
HNaY	3.0	27	48	14	10
γ-Al_2O_3	8.2	40	29	11	18
0.02 Na/γ-Al_2O_3 (see [c])	5.7	30	45	15	9
1.7 Na/γ-Al_2O_3	0.1	1.6	62	10	22
H_2SO_4/γ-Al_2O_3	0.6	14	42	15	26
Cr/SiO_2	0.33	12	38	20	22
Cr/γ-Al_2O_3	3.9	17	45	16	20
W/γ-Al_2O_3	1.66	26	52	10	11
Mo/γ-Al_2O_3	0.24	15	48	9	26
Co/γ-Al_2O_3	4.8	28	47	10	14

[a] Here and below, in mmol h^{-1} (g cat)$^{-1}$; [b] HSiW = $H_4SiW_{12}O_4$; [c] hereinafter, the value implies the content in mass %.

Table 2. Acid-base properties of some catalysts.[56]

Catalyst	BAS: [a] PA^c /kJ mol^{-1}	LAS: [a] Q_{CO}, /kJ mol^{-1}	BS: [a] PA^o, /kJ mol^{-1}
K_2WO_4/SiO_2	1170–1190 (0)	19 (2.1)	830–950 (3.0)
K_2WO_4/Al_2O_3	< 1200 (0)	31 (0.5)	800–925 (3.6)
NaX	< 1200 (0)	20 (3.0)	800–900 (0.5)
H_3PO_4/SiO_2	~1300 (1.2)	0	< 800 (–)
$HSiW/SiO_2$	< 1200 (1.0)	0	800–900 (–)
Cr/SiO_2	< 1200 (0.25)	28 (0.4)	800–900 (2.0)
HNaY	< 1200 (1.0)	20 (1.1)	800–900 (1.0)
		35–55 (0.16)	
HZSM-5	1170–1180 (0.33)	33–37 (0.16)	800–900 (1.1)
		42–54 (0.013)	
γ-Al_2O_3	1170–1270 (0.03)	32–34 (2.2)	800–900 (4.0)
		41–56 (0.2)	
0.02 $Na/Co/\gamma$-Al_2O_3	< 1200 (0)	27–32 (4.2)	850–915 (2.2)
			920–960 (0.8)
1.7 Na/γ-Al_2O_3	< 1200 (0)	18–20 (2–3)	830–960 (3.3)
Cr/γ-Al_2O_3	1245–1270 (0.15)	36 (2.4)	900 (2.8)
γ-Al_2O_3 + H_2SO_4	1170–1180 (0.1)	37–48 (0.5)	0

[a] The values in parentheses are the concentrations (C) of active sites in μmol m^{-2}; the dash means that no data on the concentration are available.

The effect of acid-base properties of the catalysts on their activity and selectivity was reported in a number of publications.[55, 56, 60, 61] The catalysts containing alkali metals or their compounds (K_2WO_4/SiO_2, K_2WO_4/Al_2O_3, Na/Al_2O_3)[55] have no BAS and contain weak LAS and strong BS. In the presence of these sites, dimethyl sulfide is formed in low yield, while the major organosulfur product is methanethiol. On the surface of NaX zeolite, there is no BAS either but there are weak LAS and medium-strength BS. It surpasses somewhat the supported alkaline catalysts in activity; the selectivity to dimethyl sulfide is somewhat higher, and methanethiol is the major product. On the surface of supported alkaline catalysts and NaX zeolite pretreated with a $H_2S + H_2$ mixture at 400 C for 1 h, a small number of strong BAS appears (C = 0.01–0.03 μmol m^{-2}), resulting in some increase in the catalyst activity and selectivity for the formation of dimethyl sulfide but this affects only slightly the selectivity to methanethiol. These catalysts are insufficiently stable during the process. For example, at 190–250 °C, the activity of NaX zeolite decreases during a reaction for 3 h by a factor of 3–10. Low stability of the activity of this catalyst is related to the necessity to use long contact times in the reaction, which promotes the formation of compounds that block the surface active sites. The activity of the K_2WO_4/Al_2O_3 catalyst also decreases with an increase in the experiment duration. The H_3PO_4/SiO_2 catalyst having no LAS and containing only weak BAS and weak BS is inactive towards the formation of methanethiol and dimethyl sulfide from dimethyl disulfide. The surface of SiO_2-supported 12th

series heteropolyacids also have no LAS, contain weak BS but also a considerable number of strong BAS. In the presence of these catalysts at 190 °C, the decomposition of dimethyl disulfide yields approximately equal amounts of thiol and sulfide. After completion of the experiment, products of extensive disulfide decomposition — sulfur, carbon and polymer deposits such as (CH_2S_n) arising on the BAS — are detected on the surface of these catalysts. The increase in the process temperature to 250 °C results in a considerable destruction of the heteropolyacid and the loss of catalytic activity. The Cr/SiO_2 catalyst containing strong BAS, weak LAS and medium-strength BS have a modest activity in dimethyl disulfide decomposition.

Considerable activity in the dimethyl disulfide transformation is displayed by hydrogen form of HNaY and HZSM-5 zeolites[60,61] containing strong BAS, strong LAS and medium-strength BS. The HNaY zeolite is less active than HZSM-5, which has a more acidic surface. The introduction of cobalt into decationized zeolites changes the reaction rate compared to that observed for the parent zeolite. The catalyst 5% CoHNaY is 2.3–3.6 times more active than HNaY, while 2% CoHZSM-5 is 2 times more active than HZSM-5. The Co^{2+} cations introduced into the channels of HZSM-5 are bound[62–64] to extra-framework Al^{3+}, which reduces the surface acidity of the catalysts containing 2% and 5% Co: the concentration of strong BAS decreases 1.6–1.7-fold and the Al^{3+}-based LAS are completely suppressed; however, strong Co^{2+}-based LAS appear and ultimately the dimethyl disulfide decomposition rate increases. The cobalt catalysts based on HZSM-5 with a Si : Al ratio of 35 and 17 somewhat differ in activity. This is due to the fact that upon the increase in the amount of Si with respect to Al, the concentration of Al^{3+} LAS decreases; correspondingly, the introduction of cobalt into a zeolite with Si : Al = 35 gives fewer strong Co^{2+} LAS. The variation of the cobalt concentration in HZSM-5 shows that a catalyst containing up to 2.5 mass % Co is 1.5–2 times more active at 250 °C than the decationized zeolite, but at higher contents of Co (3 mass % – 10 mass %), the activity decreases. Upon the introduction of up to 3 mass % Co into a high-silica zeolite, it is arranged almost completely in the zeolite channels as isolated Co^{2+} ions and one-dimensional nanocluster CoO and $CoAl_2O_3$ particles; at higher Co content, two- and three-dimensional particles also appear; in the reducing medium, Co^0 nanoparticles are also formed. During the reaction, the activity of Co-containing zeolites decreases, but the stability of this catalytic system is 2–3 times higher than that of decationized zeolites, probably, due to a reduced concentration of BAS in cobalt-containing zeolites.

The surface of γ-Al_2O_3 calcined at 500 °C bears weak BAS, a very small number of strong BAS, strong LAS and medium-strength BS.[56] The catalyst is active towards the formation of dimethyl sulfide and methanethiol from dimethyl disulfide. After treatment of γ-Al_2O_3 with a mixture of $H_2S + H_2$ at 400 °C for 1 h, the number of strong BAS on the surface increases (C = 0.08 μmol m^{-2}), the strength of LAS and BS does not change, but their concentration somewhat decreases. As compared with the initial γ-Al_2O_3, the catalyst activity and selectivity with respect to dimethyl sulfide somewhat increase, while the selectivity to methanethiol decreases. The introduction of sodium ions into γ-Al_2O_3 suppresses BAS, decreases the strength of LAS, and increases the surface basicity. As a result, the dimethyl sulfide formation rate decreases and that of methanethiol increases. The addition of sulfuric acid to γ-Al_2O_3 induces an increase in the concentration of strong BAS and an increase in the strength of LAS, but suppresses BS. The activity of this catalyst in decomposition of dimethyl disulfide is reduced.

From comparison of the catalysts with different acid-base properties, it was concluded[55] that the formation of methanethiol from dimethyl disulfide requires the presence of weak LAS and strong or medium-strength BS on the surface. For this reaction to proceed at a high rate, it is required that several types of sites (strong BAS, strong LAS and medium-strength BS) be present simultaneously on the catalyst surface. Furthermore, the surface BAS should be strong and able to protonate the disulfide at one sulfur atom, while strong LAS are required to eliminate the second sulfur atom from the disulfide molecule. The basic sites are needed for coordination to the CH_3 group; they should be of moderate strength to promote the formation of surface CH_3O groups and simultaneously do not hamper the subsequent cleavage of the bond of CH_3 groups with the surface in the complex preceding the dimethyl sulfide formation.

For the formation of dimethyl sulfide from dimethyl disulfide, it is especially important that strong LAS be present on the catalyst surface.[55] This is confirmed by the existence of a linear dependence of the logarithm of dimethyl disulfide conversion rate per LAS on the strength of these sites (Fig. 2). The addition of substances that block LAS, in particular water, to the reaction mixture induces a decrease in the selectivity to dimethyl sulfide and an increase in the selectivity to methanethiol. For example, on the Mo/Al_2O_3 catalyst at 350 °C and X = 90%, the rates of dimethyl disulfide conversion in a dry helium atmosphere and with addition of 6 vol.% of water are 37 and 22 mmol h^{-1} (g cat)$^{-1}$, respectively, the selectivity to methanethiol increases from 15% to 67% and that to

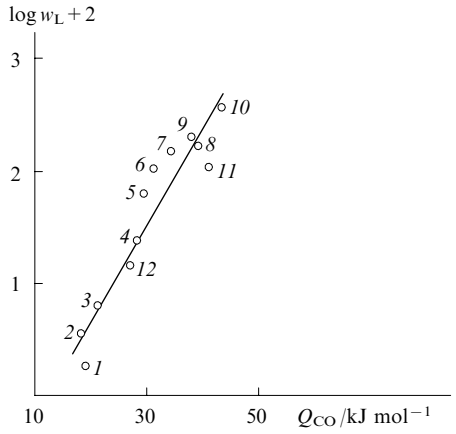
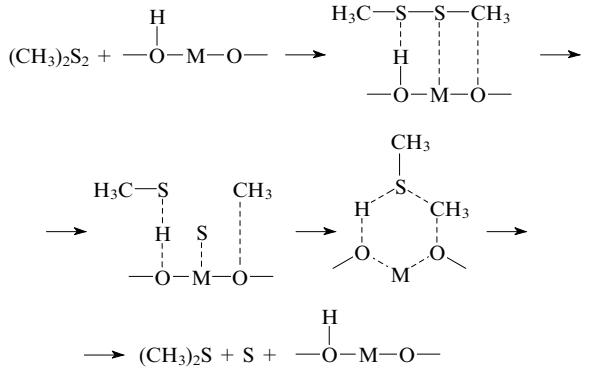


Figure 2. Logarithm of the formation rate (w_L) of dimethyl sulfide related to the total number of Lewis acid sites (L-sites) *vs.* strength of these sites (Q_{CO}) at 190 °C.[57]
Catalysts: (*1*) NaX, (*2*) 2.3% Na_2O/Al_2O_3, (*3*) MgO, (*4*)0.23% Na_2O/-Al_2O_3, (*5*) 0.04% Na_2O/-Al_2O_3, (*6*) K_2WO_4/γ-Al_2O_3, (*7*) γ-Al_2O_3 (S_{sp} = 200 m^2 g^{-1}), (*8*) γ-Al_2O_3 (S_{sp} = 275 m^2 g^{-1}), (*9*) $B_2O_3/(\gamma+\chi)$-Al_2O_3, (*10*) η-Al_2O_3, (*11*) TiO_2, (*12*) Cr/SiO_2 (S_{sp} is specific surface area).

dimethyl sulfide decreases from 75% to 20%. A similar trend is observed in the presence of other catalysts.[57, 65, 66]

Considering the properties of organic disulfides and the available adsorption data (see Section II), as well as the acid-base properties and activity relationships of the catalysts, conclusion was made[55] about the mechanism of dimethyl disulfide conversion on acid-base catalysts (Scheme 6).

Scheme 6



Dimethyl disulfide interacts with the solid catalyst to give a coordination bond between one sulfur atom of the disulfide and an acceptor site on the surface. The complexation induces cleavage of the weak S–S bonds in the disulfide and formation of methylthio groups on the surface. Upon coordination of the second disulfide sulfur atom to LAS and the methyl carbon atom to BS, the C–S bond is cleaved, and as a result, sulfur is liberated and the CH_3 group is formed. The arising CH_3S and CH_3 groups undergo various transformations, resulting in evolution of H_2S, CS_2, sulfur, methane, thioformaldehyde and resins. The CH_3S group reacts with the proton of the surface to give methanethiol. Some methanethiol molecules are condensed to give dimethyl sulfide and H_2S; this reaction occurs at a high rate on acid catalysts.[67] Dimethyl sulfide may be formed upon condensation of two CH_3S groups accompanied by sulfur release or, what is more probable, upon the reaction of CH_3S and CH_3 groups by a mechanism similar to that known for the formation of dimethyl ether upon methanol dehydration.[68]

When the reaction is carried out on oxide catalysts in helium with some amounts of H_2S added, the reaction rate and the ratio of the sulfide to thiol formed change.[53, 54, 57] As compared with experiments in pure helium, in the presence of H_2S, the selectivity to alkanethiol is higher and the selectivity to sulfide is lower (Table 3). Hydrogen sulfide participates in the process, as indicated by the fact that the conversions of disulfide and hydrogen sulfide are similar. After experiments in helium with H_2S addition, polymeric deposits and sulfur are accumulated on the catalyst surface, but the catalyst is still more stable than observed in neat helium experiments. The transformations of dialkyl disulfides in various media were also considered in a monograph.[1]

In a long-term process of disulfide conversion in the presence of Al_2O_3-supported transition metal oxides containing strong acid sites,[66–68] the initial catalyst activity increases, which is caused by sulfiding of the oxide by the reaction medium. Treatment of supported transition metal oxides with an $H_2S + H_2$ mixture at 400 °C substantially increases the activity (Table 4).[69] The metal sulfides formed upon sulfiding of oxides are partially reduced to give, on the surface, coordinatively unsaturated cations, which are strong acceptor sites.[70] Sulfiding of these catalysts at elevated temperature increases the concentration of strong BAS on the surface due to dissociative chemisorption of H_2S. The mechanism of dimethyl disulfide transformation on oxide and sulfided catalysts is supposed to be the same; in particular, dimethyl sulfide may be formed upon the

Table 4. Transformation rate of dimethyl disulfide and selectivity of product formation on sulfided catalysts.[69]

Catalyst	T/°C	w	Selectivity (%)		
			Me_2S	MeSH	H_2S
2.5 Cr/γ-Al_2O_3	190	0.60	26	34	16
	250	6.43	34	32	10
2.5 Cr/SiO_2	250	0.11	14	43	4
5 Mo/γ-Al_2O_3	190	1.35	50	16	16
	250	6.9	46	23	13
10 Mo/C	250	0.77	32	50	0
10 Mo/SiO_2	250	0.59	28	54	0
10 W/γ-Al_2O_3	190	0.20	25	60	20
	250	6.07	44	28	17
10 W/C	250	0.07	10	53	0
5 Co/γ-Al_2O_3	190	0.43	33	42	6
	250	9.03	43	34	10
5 Ni, 10 Mo/γ-Al_2O_3	190	0.67	28	42	6
	250	3.60	35	43	3
2.5 Co, 10 Mo/γ-Al_2O_3	250	1.95	29	46	2

Table 3. Comparison of the catalysts in terms of the rate of transformation of dimethyl disulfide (w) and selectivity (S) of the decomposition of dimethyl disulfide in pure helium and in helium with hydrogen sulfide additive (350 °C, conversion of dimethyl disulfide is 90%).[57]

Catalyst	In helium			In helium + 9 vol.% H_2S		
	w/mmol h^{-1} (g cat)$^{-1}$	S (%) (MeSH)	S (%) (Me_2S)	w/mmol h^{-1} (g cat)$^{-1}$	S (%) (MeSH)	S (%) (Me_2S)
SiO_2	0.3	60	6	6	78	14
HZSM-5	18	7	70	27	61	28
γ-Al_2O_3	20	11	69	146	78	14
Mg/Al_2O_3	37	15	75	140	77	12
K_2WO_4/Al_2O	17	60	30	41	71	21
K_2CO_3/SiO_2	18	76	23	52	80	14
Na/Al_2O_3	36	60	28	168	76	16

reaction of the CH_3S and CH_3 surface groups. The activity of sulfided catalysts towards the formation of dimethyl sulfide (w) is not affected by the binding energy of the sulfur atom to the surface, q_S ('sulfur mobility'). It is characterized by the temperature at which the rate of hydrogen sulfide evolution upon the hydrogen reduction of various catalysts is 0.06 mmol h^{-1} (g cat)$^{-1}$. This is illustrated, for example, by the data for catalysts containing 5 mass % of the metal supported on alumina (the dash means Al_2O_3 without additives).[69]

Metal	–	Co	Cr	Mo	W	Pd	Ni	Re
w [a]	6.1	9.7	4.7	7.0	2.8	2.0	1.7	1.0
q_S (see [b])	12.9	22.1	18.9	19.1	19.0	27.9	19.5	34.1

[a] In mmol h^{-1} (g cat)$^{-1}$; [b] in $(1/T) \times 10^4$ /K^{-1}.

The sulfided cobalt catalysts are most active in the conversion of dimethyl disulfide.[69, 71] The catalysts prepared using cobalt acetate as the precursor of the active component have advantages over catalysts based on cobalt chloride and nitrate due to higher degree of dispersion of active particles. The support nature also plays a role: alumina-supported sulfided transition metal oxides are more active than catalysts supported on carbon, silica, amorphous aluminosilicate or zeolite. The activity of alumina–cobalt catalysts increases as the Co content increases from 0.5 mass % to 10 mass % and decreases at higher Co contents; the selectivity to dimethyl sulfide does not change. As the catalyst sulfiding temperature rises from 190 to 400 °C, the disulfide conversion rate increases and then sharply decreases. The catalyst 10% Co/Al_2O_3 sulfided at 400 °C is most efficient.[69, 71] Kinetic measurements indicate [69] that in the presence of this catalyst, the selectivities of formation of any product at temperatures of 150–190 °C do not depend on the conversion value, *i.e.*, the products are formed from dimethyl disulfide along independent pathways. Above 200 °C, the selectivity to CS_2 does not change with increase in the conversion but the selectivity to methanethiol deceases and those to dimethyl sulfide and H_2S increase. It was concluded that CS_2 is formed directly from the disulfide, while dimethyl sulfide and H_2S are produced, at least partly, upon methanethiol condensation. The variation of the initial concentration of dimethyl disulfide does not change the selectivity of dimethyl sulfide formation. As the dimethyl disulfide concentration increases from 0.5 vol.% to 3.3 vol.%, the reaction rate linearly increases (first order), while at higher concentration, the rate remains unchanged (zero order), probably, due to retardation of the reaction by the disulfide. Upon temperature rise from 150 to 350 °C, the reaction rate increases, the apparent activation energy being 55 ± 0.1 kJ mol^{-1}. When the substrate has completely converted, the selectivity of dimethyl sulfide formation is 50%–60%.

2. Synthesis of thiophene

In inert medium, diethyl and dibutyl disulfides decompose at elevated temperature in the presence of some solid catalysts to give thiophene in a yield substantially exceeding that in the non-catalyzed transformation.[16, 72] The catalytic reaction gives, along with thiophene, cracked products — hydrogen sulfide, hydrogen and hydrocarbons, which are mainly ethylene and ethane in the case of diethyl disulfide and butylene and butane in the case of dibutyl disulfide; minor amounts of methane, propylene and propane are also formed. With the catalyst remaining the same, the thiophene formation rate is approximately twice higher from dibutyl disulfide than from diethyl disulfide. The disulfide conversion and the product yield increase with temperature rise and for longer contact times. The selectivities of product formation do not change as the conversion varies, indicating that thiophene formation and disulfide cracking

Table 5. Transformation of dialkyl disulfides to thiophene in the presence of sulfide catalysts.[72]

Catalyst	T/°C	Contact time /s	Thiophene yield (mol.%)	Catalyst	T/°C	Contact time /s	Thiophene yield (mol.%)
Di-n-butyl disulfide				Diethyl disulfide			
V_2O_5S [a]	525	0.6	46	V_2O_5S [a]	560	0.6	17
MoO_3S [a]	520	0.8	14	MoS_2	580	10.0	17
MoS_2	580	10	27	Fe_2O_3S [a]	450	6.0	27
Rh_2S_3	545	0.6	30	AlMo	500	3.0	12
Fe_2O_3S [a]	450	0.6	20	AlCoMo	590	1.0	17
	500	0.6	30	Cr_2O_3S/Al_2O_3 (see [a])	560	3.0	31
	540	0.6	50	AlCrK	500	6.0	30
Cr_2O_3S [a]	510	0.6	33		550	6.0	32
FeCrCs	550	3.0	35		550	5.2	30
AlNiMo	480	3.0	28		550	3.5	26
AlCrK	450	6.0	30		550	2.1	22
	500	6.0	46		580	6.0	38
	550	6.0	64	A mixture of dimethyl and diethyl disulfides			
	550	4.4	62	AlCrK	550	6.0	9
	550	3.1	56	AlCrK + butene	550	6.0	60
	550	1.5	45		550	12.0	13
	580	6	66		500	24.0	18
	600	6	70		800	24.0	19

[a] Oxides sulfided with hydrogen sulfide at 450 °C.

occur along independent pathways. The thiophene formation and disulfide cracking are first order reactions.

The cyclization of disulfides to thiophene is accelerated by both bulk and supported oxide catalysts (Table 5).[72] Oxide catalysts such as MoO_3/SiO_2, NiMoHY, FeCrK and FeCrCs accelerate most often only the decomposition of the initial disulfide; other oxide catalysts do produce thiophene but only in minor yields. In the initial reaction period, metal oxides catalyze mainly decomposition of the initial disulfide to give H_2S and hydrocarbons, while thiophene is produced in a very low yield. As the process goes on, the oxide is sulfided by the sulfur-containing reaction medium, and this increases the catalyst activity towards the thiophene formation up to values characteristic of a sulfide catalyst. For example, at $T = 580$ °C and $\tau = 3$ s, the thiophene yield varies in the following way as dibutyl disulfide is being passed through the AlCrK catalyst in the oxide and sulfide forms:

$(C_4H_9)_2S_2$ passed /mol (ml cat)$^{-1}$	0.1	0.3	0.6	0.9	1.4	1.7
C_4H_4S yield (mol.%)						
on the oxide catalyst	0	2	11	19	27	26
on the sulfide catalyst	32	29	31	29	31	29

The activity of a sulfide catalyst in the thiophene formation depends on the reactivity of sulfur on its surface, chemisorbed sulfur being most reactive.[72] The logarithm of the rate constant for thiophene formation follows a linear dependence (Fig. 3) on the 'mobility'of sulfur on the catalyst surface. Discussions of the mechanism of thiophene formation from disulfide[16, 73–76] take into account the properties of dialkyl disulfides. At high temperature, the disulfide is dissociatively chemisorbed on the catalyst surface with S–S and C–S bond cleavage to give sulfur and hydrocarbon fragments. The latter may undergo dehydrogenation, condensation and other reactions. The hydrocarbon fragments react with surface sulfur atoms to give thiophene. The disulfide reacts with the sulfur-depleted catalyst and thus restores the steady-state sulfur content of the surface. The steps of adsorption, desorption, cracking, condensation, dehydrogenation of hydrocarbon fragments and resulfiding of the catalyst proceed at a higher rate than the reaction of dehydrogenated fragments with the sulfur atom on the catalyst surface (Scheme 7).

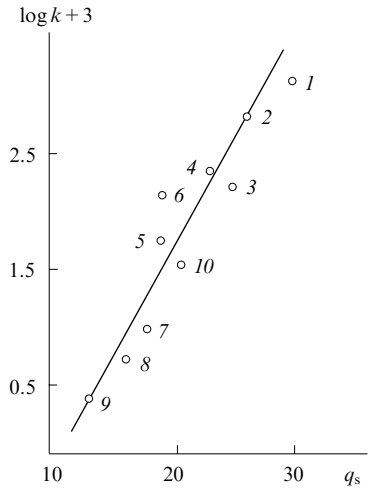


Figure 3. Logarithm of the rate constant for the thiophene formation *vs.* mobility of sulfur [$q_S = (1/T) \times 10^4/K^{-1}$] on the sulfide catalysts.[72]
(*1*) Re, (*2*) Rh, (*3*) Fe, (*4*) Mo, (*5*) Cr, (*6*) V, (*7*) W, (*8*) Zn, (*9*) Al, (*10*) Co.

Scheme 7

$$C_4H_9SSC_4H_9 \longrightarrow \left[—C—C—C—C—\right] \xrightarrow{\text{Cat [S]}} \text{Cat [ ]} + C_4H_4S$$
$$\text{Cat [ ]} + S \longrightarrow \text{Cat [S]}$$

The hydrocarbon fragments formed initially from diethyl disulfide dimerize to give C_4 intermediates and then the reaction proceeds in the same way as that with dibutyl disulfide.

The proposed mechanism was confirmed in a study of the reaction of unsaturated hydrocarbons with hydrogen sulfide. Experiments show[77] that as unsaturated hydrocarbons (butene, butadiene) in an inert gas atmosphere are passed through a sulfide catalyst at elevated temperature, thiophene is formed, the rate of this reaction being close to the rate of thiophene formation from dibutyl disulfide. Comparison of the rates of thiophene formation from butadiene and hydrogen sulfide and the assumed steps — removal of sulfur from the surface by butadiene to give thiophene and resulfiding of the catalyst with hydrogen sulfide — indicates that the rate of sulfur removal from the surface of sulfided catalyst is close to the rate of the thiophene formation from dibutyl disulfide.

The activity of catalysts for cyclization of disulfide to thiophene decreases during the reaction. The amounts of thiophene formed on various catalysts until they are completely deactivated is 0.05–0.1 mmol per m^2 of the catalyst surface. The deactivated catalyst was found to contain coke, which apparently resulted from extensive cracking of the disulfide destruction products, the coke amount constantly growing as the reaction duration increases. The coke deposition on the catalyst decreases the reaction rate and the 'mobility' of the surface sulfur. This is illustrated, for example, by the following data on dibutyl disulfide cyclization to thiophene at 520 °C on sulfided molybdenum oxide (w/w_0 is the ratio of the observed to initial reaction rates):

w/w_0 (%)	100	85	62	41	24	8
$q_S = (1/T) \times 10^4/K^{-1}$	23	20	15	10	6	2

The activity of deactivated catalysts can be restored by subjecting them to oxidative regeneration by air at 550 °C.

The catalysts most active towards thiophene formation from dialkyl disulfides are Re, Mo, Cr, Fe and platinum group metal sulfides both unsupported and supported on non-acidic alumina or aluminosilicate. Especially efficient are alumina–chromium–potassium (AlCrK) catalysts: at 540–560 °C and $\tau = 3$–6 s, they provide a thiophene yield from diethyl and dibutyl disulfides of up to 37 mol.% and 64 mol.%, respectively.

Not only single dialkyl disulfides but also their mixtures can be used for preparation of thiophene.[72] In the presence of the AlCrK catalyst at 450–600 °C and $\tau = 24$ s, a mixture of disulfides [Me_2S_2 (26%), Et_2S_2 (58%), $Pr^n_2S_2 + Bu^n_2S_2$ (15%)] isolated from gas desulfurization products was converted to thiophene and methylthiophene in 20 mol.% and 3 mol.% yields, respectively. The low yield

of thiophene must be related to the difficulty of formation of C_4 hydrocarbon fragments from dialkyl disulfides with $R = C_1-C_2$. The yield of thiophene from lower disulfides increases when C_4 hydrocarbons are added to the reaction mixture. Indeed, the transformation of a mixture of dimethyl and diethyl disulfides with a twofold molar excess of butene on the AlCrK catalyst gives thiophene in a much higher yield compared to that achieved from a disulfide mixture alone (see Table 5).

In the presence of a magnesium–chromium–alumina catalyst modified by potassium or lanthanum, thiophene is synthesized from a mixture of dialkyl disulfides with C_4 hydrocarbons [78, 79] in either a fixed or fluidized catalyst bed reactor at 400–600 °C, at a hydrocarbon to disulfide molar ratio of 1 : 1–1 : 2 and the volume rate of 400–1800 h^{-1}. The formation of thiophene from a mixture of dimethyl disulfide with butane starts above 450 °C and the thiophene yield at 550 °C reaches 90 mass %. At 550–580 °C, the catalyst operation is stable for at least 4 h, while at higher temperature, the catalyst is rapidly deactivated. The increase in the butane concentration from 10 vol.% to 30 vol.% results in thiophene yield decreasing from 90 mass % to 50 mass %. As the hydrocarbon component, butane–butene or butene–butadiene fraction can also be used. The process feedstock is a mixture of organic dialkyl disulfides (so-called disulfide oil) obtained upon purification of the propane–butane fraction from lower alkanethiols at the Orenburg gas processing plant and comprising Me_2S_2 (69.7%), MeS_2Et (24.5%) and Et_2S_2 (3.2%) or disulfide oil comprising Et_2S_2 (42%), MeS_2Et (25%), EtS_2Pr^i (15%), Me_2S_2 (3%), MeS_2Pr^i (5%), EtS_2Pr^n (3.6%), MeS_2Bu^s (0.46%), EtS_2Bu^s (0.68%) and $Pr^n_2S_2$ (0.2%). When a dimethyl disulfide mixture with butane or butadiene is used, the thiophene yield in relation to the hydrocarbon is 64 mass %–87 mass %, while a disulfide oil mixture with the butene–butadiene fraction as the feedstock gives a 60 mass %–100 mass % yield of thiophene. However, in the latter case, the catalyst stably operates only for 2 h and then the yield of thiophene decreases to 30 mass %–40 mass %. The deactivated catalyst is subjected to oxidative regeneration with air at 580 °C. The formation of similar yields of thiophene upon the conversion of C_4-hydrocarbon mixtures with dialkyl disulfides of different composition is caused by the fact that the reaction follows the above stepwise mechanism in which the role of the disulfide is reduced to the formation of hydrocarbon fragments and sulfiding of the catalyst.

IV. Catalytic hydrogenolysis of dialkyl disulfides

In the absence of a catalyst in a molecular hydrogen medium at atmospheric pressure, a 200–250 °C temperature, and gas flow rate of 2 litres h^{-1}, transformation of dialkyl disulfides scarcely takes place; at 350 °C, the conversion does not exceed 10% and the reaction products are found to contain traces of alkanethiol. Under the action of a number of solid catalysts at elevated temperature, dialkyl disulfides readily undergo hydrogenolysis.[80, 81]

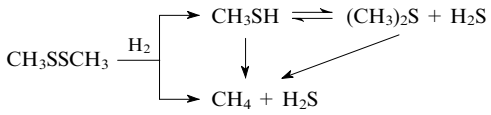
1. Hydrogenolysis of dialkyl disulfides on oxide catalysts

In the presence of zeolites of different composition in a molecular hydrogen medium, dimethyl disulfide is converted under atmospheric pressure and a temperature of 190–330 °C to give methanethiol, dimethyl sulfide, hydrogen sulfide, carbon disulfide and some methane (1 mol.%–3 mol.%).[61] In terms of the activity, zeolites can be arranged in the sequence HZSM-5 > HNaY ≫ NaX > NaY.

In a hydrogen atmosphere, the reaction rate and the selectivities of product formation are roughly the same as in a helium atmosphere.[60] The results for oxide catalysts — neat γ-Al_2O_3 and γ-Al_2O_3-supported boron and sodium oxides and potassium tungstate are also similar.[57, 82] However, in the case of other oxide catalysts, in particular, those based on transition metals, the rate of conversion of dialkyl disulfides in a hydrogen atmosphere is much higher than in an inert medium.

When industrial catalysts Co(Ni)Mo/Al_2O_3 in the oxide form are used at $p = 2-4$ MPa and 200 °C, dimethyl disulfide is hydrogenated to methanethiol in a yield of up to 70%, while at higher temperature (340–400 °C), extensive hydrogenolysis of the disulfide takes place to afford hydrogen sulfide and methane.[83–86] In solutions in heptane, octane, decane, cyclohexane and methylnaphthalene [87] at a pressure of 4 MPa and a temperature of < 150 °C, dimethyl disulfide decomposes at the S–S bond to give methylthio groups, which react with hydrogen to furnish methanethiol in a yield of ⩾ 90%. To a small extent, the C–S and C–H bonds in the disulfide are also cleaved; reactions of the fragments thus formed with hydrogen give methane and hydrogen sulfide. The rates of these reactions increase at higher temperature. At 230–330 °C, some of the methanethiol formed condenses to dimethyl sulfide with hydrogen sulfide evolution. At 330–530 °C, dimethyl disulfide is completely decomposed to produce methane and hydrogen sulfide. The reaction follows a parallel-successive chart (Scheme 8).

Scheme 8



In the presence of nickel–tungsten oxide catalysts based on Al_2O_3 or Y- and β-zeolites at $p = 3.4$ MPa, 320–360 °C, dimethyl disulfide decomposes at the C–H, C–S and S–S bonds.[88] The reaction products include hydrogen sulfide and hydrocarbons (methane on alumina-based oxide catalyst and C_4-C_5 hydrocarbons on acidic zeolite-based catalysts). After hydrogenolysis of dimethyl disulfide in various solvents, the surface of these catalysts is found to contain 0.8 mass % to 4.2 mass % of carbon depending on the solvent used and 7 mass % of sulfur. Transition metal oxides are completely converted to sulfides in this process, and this is used in industry to activate catalysts for hydrotreatment of various hydrocarbon mixtures.[89]

2. Activity of sulfide catalysts

a. Monometallic catalysts

Monometallic sulfide catalysts are active in the hydrogenolysis of dialkyl disulfides. Under the action of bulk metal sulfides in a hydrogen atmosphere, alkanethiols and dialkyl sulfides are formed. Indeed, diethyl disulfide dissolved in kerosene [90] decomposes in a static unit in the presence of bulk MoS_2 at 230 °C, a hydrogen pressure of 7–8 MPa and a reaction time (t) of 2 h to give ethanethiol and diethyl

sulfide, the yields of which are 13% and 10%, respectively, at a 76% conversion. Di-n-butyl disulfide in dioxane decomposes in the presence of bulk nickel sulfide at 150 °C and a hydrogen pressure of 3.5 MPa giving methanethiol in a yield of 73%.[91] Hydrogenolysis of dialkyl disulfides in the presence of supported sulfide catalysts has been studied in more detail. Being catalyzed by these catalysts, the hydrogenation reaction occurs at a higher rate than decomposition in a helium atmosphere. For example, the following values were obtained for the rate of hydrogenolysis of dimethyl disulfide (w) in hydrogen or helium atmosphere in the presence of alumina-supported metal sulfides at 200 °C for 50% conversion of diethyl disulfide:[82]

Metal	Mo	Pd	Rh	Ru
w/mmol h^{-1} (g cat)$^{-1}$				
in H_2	14.7	6.3	9.8	17.7
in He	0.5	1.2	2.4	2.5

The selectivity to methanethiol in the reaction carried out in helium is 53%–65%, that in hydrogen is 96%–100%.

The hydrogenolysis of dimethyl disulfide catalyzed by alumina-supported Ni, Co and Mo sulfides was studied in a flow type reactor under atmospheric pressure, a temperature of 200 °C, and a hydrogen to disulfide molar ratio of 2 : 1.[92,93] Under these conditions and at 40%–46% conversion of dimethyl disulfide, the reaction gave methanethiol and dimethyl sulfide; in none of the cases, evolution of methane was noted. These catalysts have similar activities and selectivities. According to the authors,[92,93] dimethyl sulfide is formed upon condensation of methanethiol on the support (alumina) induced by its Lewis acid sites. The addition of water to the reaction mixture blocks the sites, thus hampering the reaction. Dimethyl and dibutyl disulfides, when stirred in an autoclave in tetrahydrofuran in the presence of active carbon-supported 10% Pd sulfided under the action of the reaction medium at 75 °C and t = 0.5–4 h are mainly converted to alkanethiols, their yield reaching 95%.[94]

For decreasing the rate of formation of dimethyl sulfide upon hydrogenolysis of dimethyl disulfide, it was proposed[95–97] to use hydroxyapatite having no strong Lewis acid sites as the support for nickel, cobalt and tungsten sulfides. The dimethyl disulfide hydrogenolysis on this support modified by 5 mass % of cobalt sulfide in a hydrogen atmosphere at 360 °C affords methane and hydrogen sulfide, but at 200 °C and X = 43%–50% methanethiol is formed predominantly with a selectivity of 71%–81%. A more detailed investigation[82,98–100] demonstrated that the yield of dialkyl sulfides upon hydrogenolysis of dimethyl and diethyl disulfides is influenced by a number of factors. An important factor is the nature of the metal sulfide. Indeed, hydrogenolysis of dimethyl and diethyl disulfides catalyzed by supported Rh, Ru, Mo, Ni, Pd and W sulfides in a hydrogen atmosphere at 200 °C and X = 40%–60% results in a 0.1 mol.%–1 mol.% yield of dimethyl or diethyl sulfides, while with some low-activity catalysts, the yield increases to 2 mol.%–3 mol.%. When X > 60%, the yield of these products increases to 3 mol.%–5 mol.%, and with W/SiO_2 and W/C catalysts it increases to 10 mol.%. In the presence of metal sulfides supported on alumina or aluminosilicate, which have surface acid sites, or on SiO_2 or active carbon devoid of these sites at a dimethyl disulfide hydrogenolysis temperature of < 200 °C, the yield of dimethyl sulfide is 0.1 mol.%–0.6 mol.%, *i.e.*, the surface acidity does not influence the yield of the sulfide, this product being formed on the metal sulfide rather than on the support. However, under the action of the sulfide catalyst 5% Co/HZSM-5, dimethyl sulfide is formed in an increased yield (30%–40%), which is due to the fact that dimethyl disulfide conversion takes place on the support as well.

The yield of sulfide formed upon hydrogenation of dialkyl disulfide is affected by the concentration of the active component in the catalyst. It was found, for example, that at 200 °C, the yield of dimethyl sulfide formed on the Co/Al_2O_3 sulfide catalyst decreases with an increase in the cobalt concentration, and at > 10 mass % Co, the yield does not exceed 0.3 mol.% even at X = 96%. The dialkyl sulfide yield increases following an increase in the hydrogenation temperature and an increase in the contact time. For example, with the Co/Al_2O_3 sulfide catalyst at 240 °C, τ = 0.06 s, X = 60%, the dimethyl sulfide yield is 1.4 mol.%, while at τ = 0.18 s and X = 94%, it is 5.3 mol.%; at 180°C and X = 90%, dimethyl sulfide is not formed, and at 250 °C and X = 98%, it is formed in 3.7 mol.% yield. The reactant concentrations also play a role. With the Rh/Al_2O_3 sulfide catalyst at 200 °C, an increase in the initial dimethyl disulfide concentration from 1.5 vol.% to 5.7 vol.% induces an approximately twofold increase in the yield of dimethyl sulfide (from 1.2 mol.% to 2.5 mol.%). At a hydrogen concentration of 6 vol.%, the yield of dimethyl sulfide is 1.8 mol.%, while at a hydrogen content of 35 vol.%–65 vol.%, it is not higher than 1.0 mol.%.

The hydrogenolysis processes of dimethyl and diethyl disulfides in the presence of transition metal (Rh, Ru, Mo, Pd, Ni, W) sulfides on various supports show similar regularities.[82,98] At 200 °C and X = 40%–60%, reductive cleavage of the disulfides takes place on any of the catalysts to give mainly alkanethiols. Only minor quantities of dimethyl or diethyl sulfide and hydrogen sulfide are formed and no hydrocarbon formation is observed. At higher temperature, extensive hydrogenolysis of disulfides takes place with evolution of methane from dimethyl disulfide or ethylene from diethyl disulfide; the selectivity to ethanethiol decreases (Fig. 4). As follows from kinetic measurements,[98] the characteristics of disulfide hydrogenolysis are affected by reactant concentrations. For example, in the presence of the sulfide Rh/Al_2O_3 catalyst, the rate of the reaction performed in pure hydrogen at 200 °C increases in direct proportion to the current concentration of dimethyl disulfide increasing from 0.6 vol.% to 1.6 vol.%, while at higher concentration it remains almost constant. With the concentration of dimethyl disulfide being invariable, the increase in the initial hydrogen concentration in helium from 6 vol.% to 15 vol.% induces the reaction rate to increase, while at higher hydrogen concentration, the reaction rate does not change in this case. The rate of disulfide hydrogenation grows with temperature.

The activity of catalysts towards hydrogenolysis of dialkyl disulfides depends on their composition.[1,82,98] The quantitative comparison of the activities of monometallic sulfide catalysts in hydrogenolysis of dimethyl and diethyl disulfides with S–S bond cleavage was made at 200 °C. In the presence of Rh sulfide on various supports, Mo and Ni

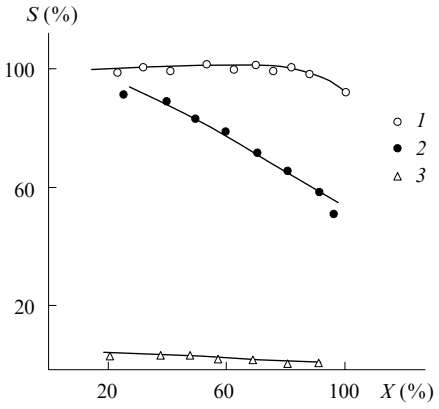


Figure 4. Selectivity of formation of ethanethiol upon hydrogenation of diethyl disulfide *vs* conversion catalyzed by sulfided 5% Pd/Al_2O_3 at temperatures of 200 (*1*), 250 (*2*), 350 °C (*3*).[82]

sulfides on silica or Ru, Pd and W sulfides on carbon, hydrogenolysis of dimethyl and diethyl disulfides occurs at similar rates, but with other catalysts the hydrogenation rate of diethyl disulfide is 1.4–6.2 times higher than that for dimethyl disulfide. Alumina-supported metal sulfides are most active (with rare exceptions) towards hydrogenolysis of both disulfides. The catalyst activity is not related to the reaction on the support. Pure Al_2O_3 shows a higher activity than other supports (5 times higher than aluminosilicate and 20–30 times higher than SiO_2 or carbon). However, the disulfide conversion rate on Al_2O_3 is substantially (4–10-fold) lower than in the presence of sulfide catalysts based on it, and Rh, Ru, Ni and W sulfides supported on Al_2O_3 are only 1.2–3.1 times more active than on other supports. The change in the activity of sulfide catalysts based on various supports is not related to different degrees of dispersion of the metal sulfide; also, no considerable influence of the protic and aprotic acidity of the catalyst surface on the activity towards hydrogenolysis of dialkyl disulfides was revealed. The activities of a series of supported sulfide catalysts depend appreciably on the metal content of the support.

Indeed, upon the increase in the nickel content on Al_2O_3 from 2.5 mass % to 10 mass %, the hydrogenolysis rate increases 3-fold. However, the increase in the Mo content on Al_2O_3 from 5 mass % to 19.5 mass % has little influence on the activity. With the Co/Al_2O_3 sulfide catalyst, the dimethyl disulfide conversion rate grows as the cobalt content increases from 1 mass % to 8 mass %,[99–102] while at higher Co contents it no longer changes. The specific activity (the rate in relation to 1 g of Co) sharply decreases as the Co content increases from 1 mass % to 6 mass % but then the decrease slows down, which is due to the change in the degree of dispersion of the active component.

In some cases, the catalyst activity is affected by the nature of the precursor of the active component. The activity of the monometallic Ni and Co sulfide catalysts does not depend on the precursor of the active compound (chloride or nitrate). With the 10% Mo/Al_2O_3 sulfide catalyst obtained using phosphomolybdic acid, the reaction rate is 1.7 times higher than with the sample prepared from ammonium heptamolybdate. Cobalt catalysts prepared from cobalt chloride, nitrate and acetate differ somewhat in the activity but the method of deposition of the cobalt precursor on the support is more significant. Indeed, a 10% Co/Al_2O_3 sample obtained from Co nitrate, which was converted to cobalt hydroxide on the surface, was 1.7–2 times as active as the catalysts obtained by impregnation with the salt. The higher activity of the samples prepared by this method or using cobalt acetate is due to the 10 times smaller size of Co-containing particles of the precursor on the support surface. The activity of sulfide catalysts increases after they have been partly reduced by hydrogen at 200–300 °C, which is related to an increase in the concentration of coordinatively unsaturated cations needed for hydrogenation of disulfide to alkanethiol.

While interpreting the mechanism of dialkyl disulfide hydrogenolysis, researchers[92] proposed that the selective hydrogenolysis of disulfide with S–S bond cleavage giving alkanethiol requires disulfide and hydrogen activation. When dimethyl disulfide is adsorbed on a partly reduced metal sulfide surface, one sulfur atom of the disulfide is hydrogen-bonded to the proton of surface SH groups, while the other sulfur atom reacts with the hydride ion resulting from the heterolytic decomposition of molecular hydrogen. The transformation of this surface structure affords two methanethiol molecules and releases the coordinatively unsaturated metal ions. However, it was suggested in another study[99] that the mechanism of dialkyl disulfide hydrogenolysis to give alkanethiols is similar to that proposed for the reaction in an inert gas atmosphere (see above).

b. Bimetallic catalysts

Bimetallic sulfide catalysts are much more active towards hydrogenolysis of various sulfur compounds than monometallic sulfide catalysts. In particular, bimetallic sulfide catalysts are active in the hydrogenolysis of dialkyl disulfides at the S–S bond yielding alkanethiols. It was ascertained[92,93] that the $Ni,Mo/Al_2O_3$, $Ni,W/Al_2O_3$ and $Co,Mo/Al_2O_3$ catalysts have 2–3.5 times higher specific activities (first order reaction rate constant per gramme of the catalyst) at 200 °C than monometallic catalysts, namely, Al_2O_3-supported Ni, Co and Mo sulfides. With the $Ni,Mo/Al_2O_3$ sulfide catalyst, the yield of dimethyl sulfide continuously grows as the dimethyl disulfide conversion increases, while the yield of methanethiol grows only to a certain limit and then diminishes, which attests to consumption of methanethiol *via* condensation. Probably, the condensation takes place on the support, namely, alumina, which has Lewis acid sites on the surface, because addition of H_2S or water to the reaction mixture blocks these sites and hampers the formation of dimethyl sulfide. A study of hydrogenation of dimethyl disulfide at 200 °C in the presence of sulfided catalysts obtained by introducing cobalt molybdate into calcium-deficient hydroxyapatite or molybdenum into cobalt-containing hydroxyapatite demonstrated[96] that the activity of the sulfide catalyst based on calcium-deficient apatite depends on the atomic ratio Co : (Co + Mo) and reaches a maximum when this ratio is 0.3. In the presence of this catalyst, the selectivity of methanethiol formation is 100% and 92% for dimethyl disulfide conversion of 50% and 100%, respectively. On the pure support having no LAS, the condensation of methanethiol to dimethyl sulfide barely takes place.

The regularities of selective hydrogenolysis of dimethyl disulfide to methanethiol in the presence of bimetallic sulfide catalysts of various compositions have been studied

in detail.[101] Below 200 °C they are the same as for monometallic catalysts: at a disulfide conversion of 60%–80%, the selectivity to methanethiol is 100%, while at higher conversion it somewhat decreases and small quantities of dimethyl sulfide and hydrogen sulfide are detected in the reaction products. As the temperature is raised to 220–250 °C, the yields of the latter products increase and the selectivity to methanethiol somewhat decreases. The selective hydrogenolysis is a first-order reaction. The rate constant for the reaction increases as the temperature is raised from 160 to 250 °C. When the temperature is raised to 360–400 °C, the hydrogenolysis of dimethyl disulfide not only involves the S–S bond to give mainly methanethiol, but extensive hydrogenolysis with C–S bond cleavage giving methane and H_2S also takes place (Fig. 5). Presumably, at higher temperature, the reaction follows a consecutive mechanism: first the dimethyl disulfide hydrogenolysis with S–S bond cleavage occurs and then the resulting methanethiol and dimethyl sulfide undergo hydrogenolysis with C–S bond cleavage. The C–S bond is also cleaved in the parent disulfide but this makes a minor contribution to the overall hydrogenolysis process.

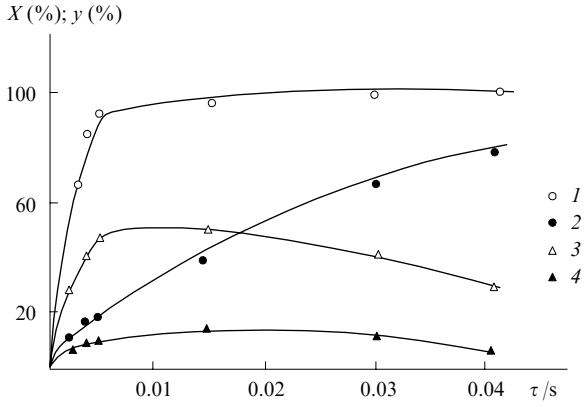


Figure 5. Effect of the contact time on the conversion (*X*) of dimethyl disulfide (*1*) and yields (*y*) of methane (*2*), methanethiol (*3*) and dimethyl sulfide (*4*) upon hydrogenolysis of dimethyl disulfide with C–S bond cleavage on the 2.5 Co,10 Mo/Al_2O_3 sulfide catalyst at 380 °C.[101]

A quantitative comparison of the activities of bimetallic sulfide catalysts towards disulfide hydrogenolysis with S–S bond cleavage was based [1, 82, 101] on the decomposition rate of dialkyl disulfides during their conversion providing 100% selectivity to alkanethiol. For equal contents of the supported metals, the Ni,Mo/Al_2O_3 sulfide catalysts were at least twice more active in the hydrogenolysis than Co,Mo/Al_2O_3. The activities of the bimetallic sulfide catalysts for dialkyl disulfide hydrogenolysis with S–S bond cleavage to give alkanethiol at temperatures below 200 °C are affected by the catalyst composition and preparation procedure, the nature of the active component precursor, the content of the active component and heat treatment conditions.[101] The catalyst prepared by co-deposition of nickel and molybdenum is 1.5 more active than that prepared by successive deposition of Co and Mo. The activity of Ni,Mo/Al_2O_3 sulfide catalysts depends on the nature of the support, the highest activity being on Al_2O_3, a 3.3 times lower activity being on aluminosilicate and 17 times lower activity being on SiO_2 and the carbon support. The catalysts based on phosphomolybdic acid and nickel nitrate have 1.3 times higher specific activities than the samples prepared based on ammonium heptamolybdate and nickel chloride. The activity of bimetallic catalysts prepared by co-deposition of nickel and molybdenum is the same or higher than in the case of separate deposition. The specific activity of alumina–nickel–molybdenum catalysts depends on the Ni:(Ni+Mo) atomic ratio: for ratios of 0.2–0.3, it is higher than for 0.4–0.6 or <0.2. A comparison of the atomic catalytic activities of mono- and bimetallic catalysts shows that in the hydrogenolysis of diethyl disulfide, this value for Ni,Mo/Al_2O_3 exceeds the sum of atomic catalytic activities of the monometallic catalysts Ni/Al_2O_3 + Mo/Al_2O_3 by a factor of 1.2–1.3; for other sulfide catalysts, the sum of atomic catalytic activities of monometallic catalysts is equal to or higher than the activity of the corresponding bimetallic catalyst (Table 6). In the extensive hydrogenolysis of dimethyl disulfide at the C–S bond with evolution of methane and H_2S at 360–400 °C, the specific catalytic activity of the Co,Mo/Al_2O_3 sulfide catalyst is also approximately equal to the sum of activities of monometallic catalysts.

Thus, in comparison with hydrogenolysis reactions of other organic sulfur compounds, for example, thiophene, the conversion of dimethyl disulfide catalyzed by bimetallic Ni(Co),Mo/Al_2O_3 catalysts with S–S and C–S bond cleavage demonstrates only minor synergistic effect. Therefore, the mechanism of both selective and extensive hydrogenolysis of dialkyl disulfides cannot be interpreted from the standpoint of concerted mechanism proposed for thiophene hydrogenolysis,[103, 104] in which the key role is allocated to the presence of occluded hydrogen in the active

Table 6. Specific activity of mono- (MMC) and bimetallic (BMC) sulfide catalysts in hydrogenolysis of dimethyl disulfide at the S–S bond to give methanethiol.[101]

Content of active components on Al_2O_3 (mass %)	*T*/°C	Atomic catalytic activity		Content of active components on Al_2O_3 (mass %)	Atomic catalytic activity *T* = 190 °C	
		BMC [a]	MMC [b]		BMC [a]	MMC [b]
2.5 Co,10 Mo	190	8.9	9.3	2.5 Ni,10 Mo	12.6	7.2
	200	9.5	10.5	3.6 Ni,12.8 Mo	13.2	5.0
	380	43.9 [c]	41.9	5 Ni,10 Mo	10.2	4.6
	400	65.7 [c]	59.1	10 Ni,10 Mo	8.7	4.6

[a] Rate constant (*k*) in litres of gas s^{-1} (g-atom M)$^{-1}$, where M is the sum of metals; [b] overall *k* in litres of gas s^{-1} (g-atom M)$^{-1}$ for monometallic catalysts, Co(Ni)/Al_2O_3 + Mo/Al_2O_3; [c] here the catalyst activity is given for hydrogenolysis at the C–S bond with methane and H_2S evolution.

component of the sulfide catalyst. This hydrogen is present in bimetallic sulfide catalysts and in monometallic catalysts (Ni/Al_2O_3 and Mo/Al_2O_3) but is absent from the monometallic Co/Al_2O_3 sulfide catalyst. However, the Co/Al_2O_3 catalyst shows high activity in the disulfide hydrogenolysis both at the S–S bond and the C–S bond and its specific activity exceeds that achieved with Ni/Al_2O_3 and Mo/Al_2O_3 catalysts, which contain occluded hydrogen. The specific activity of the bimetallic $Co,Mo/Al_2O_3$ catalyst containing occluded hydrogen is equal to or even somewhat lower than the overall activity of monometallic $Co/Al_2O_3 + Mo/Al_2O_3$ catalysts, while bimetallic $Ni,Mo/Al_2O_3$ catalysts show only slight increase in the specific activity with respect to the monometallic $Ni/Al_2O_3 + Mo/Al_2O_3$ sulfide catalysts. Hence, it was concluded [101] that hydrogenolysis of dialkyl disulfides on bimetallic sulfide catalysts follows the same mechanism as the reactions in the presence of monometallic sulfide catalysts (see above).

V. Catalytic oxidation

In the absence of a catalyst in an oxygen atmosphere, dialkyl disulfides undergo destructive oxidation at elevated temperature. For example, heating of dimethyl disulfide in oxygen at 240 °C affords sulfur and carbon dioxides, formaldehyde and methanol; the reaction follows a radical mechanism.[105] The process route changes in the presence of catalysts, the reaction rate being dependent on the catalyst nature and reaction conditions. The interaction of the disulfide with the catalyst can activate the sulfur atoms with either retention of the bonds in the molecule or cleavage of the S–S and C–S bonds. In the former case, oxygen atoms may add to one or both sulfur atoms to give mild oxidation products — alkylthiosulfinates and alkylthiosulfonates. In the latter case, the oxygen atoms add to the RS fragment arising upon S–S bond cleavage, resulting in the formation of alkanesulfonic acid, or destructive oxidation of the disulfide takes place with evolution of sulfur dioxide as the major sulfur-containing product.

The destructive oxidation of dimethyl and diethyl disulfides occurs at temperatures of >400 °C and gives sulfur and carbon oxides, carbon disulfide and water. This reaction can be catalyzed by $CuO-MoO_3/Al_2O_3$,[106, 107] Cu–Mo–Cr,[108] MnO/FeO_3,[109] La–Ba–Ni [110] and Pt/Al_2O_3.[111] In the gas phase at 220–260 °C, atmospheric pressure and high oxygen content in the presence of bulk V, Cr and Cu oxides, diethyl disulfide mainly undergoes extensive oxidation.[72] The major sulfur product of this reaction is sulfur dioxide, the selectivity of its formation being 91%–99%. The yield of SO_2 increases with temperature rise and with an increase in the contact time. A decrease in the oxygen content in the system leads to lower disulfide conversion and lower yield of sulfur dioxide; also, partial oxidation products — ethylthiosulfinate, ethylthiosulfonate and ethanesulfonic acid — are formed in minor quantities (Table 7). Much greater quantity of the products of partial oxidation of dialkyl disulfides is formed when the catalytic reaction is performed in the liquid phase with hydrogen peroxide or oxygen as the oxidant.

The oxidation of dimethyl and diisobutyl disulfides with hydrogen peroxide in the presence of sodium tungstate or molybdate [112, 113] is carried out at 20–60 °C for 2–3 h in chloroform, benzene, hexane or diethyl ether with phase transfer catalysts — benzyltriethylammonium or cetyltrimethylammonium bromide; this gives thiosulfonate, thiosulfinate and sulfonic acid. The active species of this catalytic system is the peroxotungstate or peroxomolybdate that formed in the reaction medium. The oxidation of dialkyl disulfide is stepwise (Scheme 9).

Scheme 9

$$CH_3SSCH_3 \xrightarrow{[O]} CH_3SS(O)CH_3 \xrightarrow{[O]} CH_3SS(O)_2CH_3$$

In chloroform at 20 °C within 2 h, the yield of methylthiosulfinate is 49%, that of methylthiosulfonate is <2%–3%; in the presence of an excess of hydrogen peroxide with respect to disulfide (100 : 1), the sulfonate is oxidized to disulfone $[CH_3S(O)_2S(O)_2CH_3]$. Diisobutyl disulfide at 20–50 °C, t = 1.5 h is oxidized to afford mainly isobutylthiosulfonate in a 59% yield even with a large excess of hydrogen peroxide; the disulfone yield does not exceed 5%. In the presence of iron or manganese phthalocyanines, sodium tungstate and phase transfer catalysts,[114] dimethyl and dibutyl disulfides in acetonitrile are oxidized with hydrogen peroxide at 20 °C, t = 6 h to alkylthiosulfonates (the yield of methylthiosulfonate is 41%–45% and that of

Table 7. Conversion of diethyl disulfide and selectivity of product formation upon oxidation of diethyl disulfide in the presence of oxide catalysts in the gas phase (p = 0.1 MPa).[72]

Catalyst	T/°C	τ/s	X (%)	S (%) [a]		Catalyst	T/°C	τ/s	X (%)	S (%) [a]	
				MO [b]	SO_2					MO [b]	SO_2
$O_2 : Et_2S_2$ = 100 : 1						$O_2 : Et_2S_2$ = 5 : 1					
V_2O_5	180	5.7	10	60	38	V_2O_5	220	6.7	19	36	63
	220	2.8	31	10	91		220	18	34	12	90
	220	5.2	75	1	96	$VOSO_4$	220	2.3	25	80	0
	220	17.4	83	0	99	$CuCl_2/SiO_2$	220	14.0	24	28	50
	260	2.4	50	1	98	$VO(acac)_2/SiO_2$ (see [c])	220	2.6	6	27	0
K/V_2O_5	220	6.1	35	21	78	$HSiW/SiO_2$	180	6.0	8	98	0
CuO	200	6.0	63	6	49		220	19.6	26	52	25
Cr_2O_3	200	6.2	40	13	86	$CuSO_4$	220	14.8	56	17	41

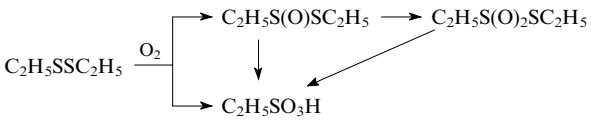
[a] Slight amounts of ethanesulfonic acid with S = 0.5%–10% were detected; [b] MO is the total selectivity to mild oxidation products $[RS(O)SR + RS(O)_2SR]$; [c] acac is acetylacetonate.

butylthiosulfonate is 61%–68%). The partial oxidation of dimethyl and di-*tert*-butyl disulfides with hydrogen peroxide also proceeds in the presence of CH_3ReO_3, the active form of the catalyst being a peroxorhenium derivative. Dimethyl and di-*tert*-butyl disulfides are oxidized at room temperature in aqueous acetonitrile and at catalyst : disulfide molar ratio of 0.1 : 1, $t = 1$ h to give primarily thiosulfinate, which is then oxidized to thiosulfonate and sulfonic acid.[115] According to a publication,[116] diethyl, di-n-propyl, di-n-dibutyl disulfides are oxidized under the action of hydrogen peroxide with a methylthioxorhenium additive in acetonitrile at 20 °C, a catalyst to disulfide molar ratio of 0.01 : 1 over a period of 1 min to give alkanesulfonic acids in 80%, 90% and 87% yields, respectively. Under the action of hydrogen peroxide with added vanadyl acetylacetonate [$VO(acac)_2$], di-*tert*-butyl disulfide in chloroform is oxidized at 15–20 °C, $t = 20$ min to thiosulfonate in a yield of 81%–93%.[117] The addition of methanesulfonic acid to hydrogen peroxide increases the yield of the product of partial oxidation of dimethyl disulfide to 95% at 85 °C.[118]

The liquid-phase oxygen oxidation of dimethyl, diethyl and dibutyl disulfides to sulfonic acid is accelerated by nitrogen oxides and nitric acid.[119, 120] The catalyst is N_2O_4; during the reaction, it is converted to N_2O_3, which is again oxidized with oxygen to N_2O_4. In the absence of oxygen and at a high content of the N_2O_4/C catalyst, di-n-propyl, diisopropyl and di-n-dibutyl disulfides in dichloroethane at 10–20 °C are converted to thiosulfonates in 95%–98% yields.[121]

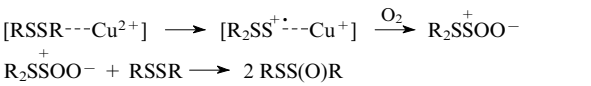
The partial oxidation of disulfides with molecular oxygen under the action of metal compounds has been described in a number of publications. According to a patent,[122] in benzene, chlorobenzene or dichloroethane in the presence of $MoCl_5$, $MoCl_4$, $MoOCl_2$, $MoOCl_3$, WCl_3, WOCl or $VOCl_3$ at 25–80 °C and under atmospheric or elevated pressure, diethyl disulfide is oxidized with oxygen to ethylthiosulfonate; at $X = 25\%–30\%$, the selectivity is 40%–85%. Vanadyl acetylacetonate is an efficient catalytic system for the partial oxidation of diethyl disulfide with oxygen.[72, 123–125] In dichloroethane at 120–140 °C, $t = 30–60$ min, the disulfide conversion is 37%–52%, while the overall selectivity to ethylthiosulfinate and -sulfonate is 50%–96%, and ethanesulfonic acid is also formed (Table 8). As the disulfide conversion increases, the selectivity to thiosulfinate decreases, while that to thiosulfonate increases; the selectivity to sulfonic acid virtually does not depend on the disulfide conversion. The partial oxidation reaction with this catalyst is depicted in Scheme 10.

Scheme 10



The liquid-phase partial oxidation of disulfides with oxygen catalyzed by transition metal complexes follows the mechanism proposed for the oxidation of dialkyl sulfides to sulfoxides and sulfones.[126] Under conditions where the complex formation with the catalyst does not induce bond cleavage in the disulfide molecule, electron density redistribution on the sulfur atom takes place giving rise to a positive charge, for example, when the oxidation is carried out in the presence of copper(II) compounds. In the oxidative medium, the radical cation is converted to peroxide, which reacts with disulfide affording thiosulfinate; then the latter is oxidized by thiosulfonate by a similar mechanism. The copper ion reduced upon complex formation is oxidized again with oxygen (Scheme 11).

Scheme 11



Under the action of $CuCl_2$ in aqueous sodium hydroxide mixed with isooctane at 60 °C, atmospheric pressure and $t = 10$ min, diethyl disulfide is oxidized at a high rate to ethanesulfonic acid.[127] At complete conversion of the disulfide, the yield of $EtSO_3H$ is 29% and sulfuric acid is also formed in a 70% yield. The proper catalyst is copper hydroxide $Cu(OH)_2$, which is formed upon the reaction of alkali with copper chloride.

In the presence of V, Cr and Cu oxides, the oxidation of diethyl disulfide[112, 123–125] under an air pressure of 5 MPa (140 °C, $t = 1–2$ h) results in the formation of ethanesulfonic acid in a 100% yield. It was ascertained by EPR and

Table 8. Conversion of diethyl disulfide and selectivity of product formation in the catalytic liquid-phase oxidation of dialkyl disulfides with air oxygen.[72]

Catalyst	T/°C	t/min	X (%)	S (%)		Catalyst	T/°C	t/min	X (%)	S (%)	
				MO[a]	RSO_3H					MO[a]	RSO_3H
In acetone						In acetone					
V_2O_5	140	120	96	0	100	$FeCl_2$	140	20	100	0	100
V_2O_4	140	60	100	0	100	$VOCl_2$	140	20	100	1	98
Cr_2O_3	140	60	95	0	100	$VO(acac)_2$	120	60	92	1	97
Cation exchanger	140	60	100	0	100		140	15	71	1	85
Cation exchanger[b]	150	60	97	0	100	In dichloroethane					
$CuCl_2$	140	15	100	8	80	$VO(acac)_2$	120	60	45	96	4
$CuCl_2$ (see[b])	140	15	84	2	98		140	60	52	93	6
$CrCl_3$	140	60	100	0	100	$VO(acac)_2$ (see[b])	150	120	37	95	0

[a] MO is the total selectivity to mild oxidation products ($RS(O)SR + RS(O)_2SR$); [b] here the oxidation of disulfide concentrate.

atomic absorption spectroscopy that the solution contains vanadium, copper and chromium ions, which are formed upon dissolution of the oxides in the reaction mixture. The reaction is assumed to proceed both on the solid oxide surface and in solution under the action of metal ions. The predominant formation of ethanesulfonic acid upon the oxidation of diethyl disulfide with oxygen is also observed in the presence of metal chlorides. The rate of formation of sulfonic acid (w) at incomplete disulfide conversion depends on the nature of the metal:

Metal chloride	$FeCl_3$	$CuCl_2$	$CrCl_3$	$MnCl_2$	$CoCl_2$	$NiCl_2$	$ZnCl_2$
w /mol litre^{-1} h^{-1}	0.63	0.23	0.18	0.14	0.11	0.05	0

In the presence of metal chlorides or cation exchange resin in acetone at 120–140 °C, the selectivity to ethanesulfonic acid for diethyl disulfide oxidation is 80%–100% (see Table 8). The oxidation has an induction period after which the reaction rate sharply increases due to the additional effect of the sulfonic acid product. Thus, depending on the conditions of the liquid-phase reaction, it is possible to obtain predominantly either alkyl thiosulfinates and alkylthiosulfonates formed as mild oxidation products or alkanesulfonic acid formed as the product of more extensive oxidation.

The partial oxidation can also be performed for mixtures of dialkyl disulfides (see Table 8). Under the action of vanadyl acetylacetonate in dichloroethane, the oxidation of a mixture of dialkyl disulfides (23% dimethyl disulfide, 54% diethyl disulfide, 22% dipropyl disulfide) formed upon gas demercaptanization afforded mild oxidation products in an overall yield of 95 mol.%, while in the case of copper chloride or cation exchange resin as the catalyst, a mixture of sulfonic acid was formed in a 100% yield.

VI. Thioalkylation with dialkyl disulfides

1. The addition of dialkyl disulfides to unsaturated compounds

Dialkyl disulfides react with unsaturated compounds to give organic sulfides. These reactions are catalyzed by metal complexes.[128–130]

The addition of dialkyl disulfides to compounds with one double bond furnishes bis(alkylthio) derivatives. For example, it was found[131] that dimethyl and diethyl disulfides add to *cis*- or *trans*-but-2-enes in the presence of the $BF_3 \cdot Me_2O$ catalyst giving rise to 2,3-bis(alkylthio)butanes (Scheme 12).

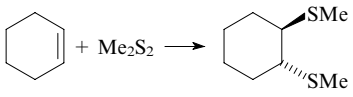
Scheme 12

$$MeCH{=}CHMe + R_2S_2 \longrightarrow MeCH(SR){-}CHMe(SR)$$

R = Me, Et

The reaction occurs at room temperature with a twofold molar excess of the alkene with respect to the disulfide over a period of 1 h, the bis(alkylthio) derivatives being formed in 90%–96% yield. The reaction with diisopropyl disulfide gives a lower yield of a bis(thio) derivative (20%–76%), while di-*tert*-butyl disulfide does not perform thioalkylation at all. Dimethyl disulfide reacts with propene or with 3-methylbut-1-ene to afford bis(alkylthio) derivatives in low yields (5%–8%). Dimethyl, diisopropyl and dibutyl disulfides react with styrene under the action of the CuI–bipy complex (bipy is 2,2′-bipyridine) in a mixture of dimethylformamide with acetic acid in the presence of air at 90 °C and t = 20–36 h producing 1,2-acetoxy sulfides in a yield of 61%–67%.[132] In the presence of the ruthenium chloride complex with cycloocta-1,5-diene or cyclopentadiene, dimethyl and dibutyl disulfides react with 2-bornene.[133] In toluene at 100 °C and t = 8 h under argon, bis(alkylthio) derivatives are formed in 84%–96% yield. Oct-1-ene reacts with disulfides at higher temperature, the formation of products of addition to cyclohexene is difficult. Dimethyl disulfide adds to cyclohexene under the action of $BF_3 \cdot Me_2O$ at 20 °C and t = 1 h to give *trans*-1,2-bis(methylthio)cyclohexane in a 81% yield (Scheme 13).[131]

Scheme 13



Aluminium and iron chlorides[134] accelerate the addition of dimethyl disulfide to the cyclohexene double bond to give bis(methylthio)cyclohexane. In toluene at room temperature and t = 20–24 h, the product yield is 42% for $FeCl_3$ and 68% for $AlCl_3$. In the presence of $SnCl_4$, dimethyl disulfide adds to cyclohexene in chloroform at room temperature affording 1,2-bis(methylthio)cyclohexane the yield of which after t = 100 h is 88%.[135] Montmorillonite-supported Zn, Cu and Fe chlorides accelerate the addition of dimethyl disulfide to cyclohexene.[136, 137] The reaction proceeds in dichloroethane or chlorobenzene at 20 °C and t = 8 h to give 1,2-*trans*-bis(methylthio)cyclohexane. The metal chloride or the pure support do not accelerate the reaction. Montmorillonite-supported metal chlorides differ in the activity.

Metal chloride	$ZnCl_2$	$FeCl_3$	$FeCl_2$	$CuCl_2$
Product yield (%)	87	75	63	60

The reaction of dialkyl disulfides with diene hydrocarbons leads to bis(alkylthio)alkenes. With the $BF_3 \cdot Me_2O$ catalyst, the reaction of dimethyl disulfide with butadiene gives *trans*-1,4-bis(methylthio)but-2-ene in a 52% yield (Scheme 14).[131]

Scheme 14

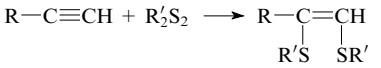
$$CH_2{=}CH{-}CH{=}CH_2 + (CH_3)_2S_2 \longrightarrow CH_3SCH_2CH{=}CHCH_2SCH_3$$

In the case of addition of dimethyl disulfide to cycloocta-1,5-diene or cyclopentadiene, the yields of bis(methylthio) derivatives are 18%–45%. In the presence of the $ZnCl_2$/montmorillonite catalyst at 20 °C, dimethyl disulfide can add to cyclohexa-1,3-diene giving a mixture of *trans*-1,2 and *trans*-1,4 derivatives in >75% yields.[136, 137] When dimethyl disulfide homologues R_2S_2 (R = Et, Pr^n, Bu^n) are used, the thioalkylation proceeds more slowly and the yield of addition products does not exceed 50%. In the presence of $RhH(PPh_3)_4$, *p*-tolylphosphine and trifluoromethanesulfonic acid,[138] diethyl, dipropyl and dibutyl disulfides add to the allenes $R{-}CH{=}C{=}CH_2$

(R = n-C_7H_{15}, n-C_5H_{11}) to give (alkylthio)alkenes in 41%–47% yields.

The reactions of dialkyl disulfides with alkynes produce compounds with a double bond (Scheme 15).

Scheme 15



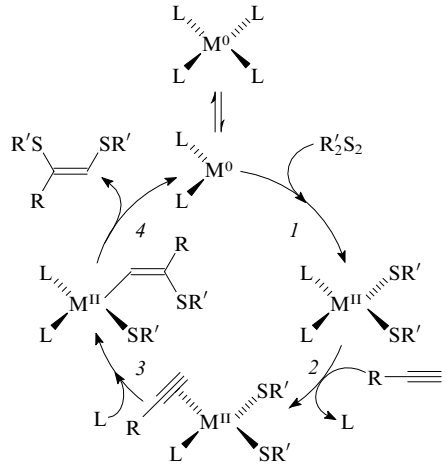
In the presence of the rhodium phosphine complex $RhH(PPh_3)_4$ and $(4\text{-}MeOC_6H_4)_3P$ with some trifluoroacetic acid added, dialkyl disulfides in acetone add to acetylene hydrocarbons to form, after refluxing for 10 h, 1,2-bis(alkylthio)-substituted alkenes.[139] The product yields depend on the structure of the substituent R in the acetylene molecule.

R	Yield (%)	R	Yield (%)
n-C_6H_{13}	95	Bu^t	91
n-C_8H_{17}	98	Bn	99
cyclo-C_6H_{11}	83	Ph	62
$Bu^nCH(Et)$	85	4-MeC_6H_4	77

The structure of dialkyl disulfide has little influence on the yields of thioalkylation products, the yields of the addition products formed in the reactions of oct-1-yne with diethyl, di-n-propyl and di-n-butyl disulfides being 93%–96%. The rhodium complex with 1,1′-bis(diphenylphosphino)ferrocene (dppf) [$RhH(PPh_3)_4$ + dppf] catalyzes the addition of di-n-butyl disulfide to oct-1-yne upon refluxing in acetone for 4 h affording bis(butylthio)octene in 61% yield.[140] With the same complex as the catalyst, dimethyl and dibutyl disulfides react with acetylene derivatives RC≡CH (R = Et_3Si, Pr^i_3Si, 2,4,6-$Me_3C_6H_2$) when refluxed in acetone for 1 h giving thio-substituted acetylene derivatives, their yields being 62%–96%.[141] When the solution contains a mixture of disulfides with various substituents, the exchange by hydrocarbon groups to give mixed disulfides can proceed under the action of the rhodium phosphine complex.[142, 143] The addition of dimethyl, di-n-propyl and di-n-butyl disulfides to hex-1-yne either unsubstituted or substituted with Ph, OH, OMe, $SiMe_3$, CH_2NMe_2 or $C_6H_{10}OH$ occurs in the presence of Ni or Pd acetylacetonate and furnishes bis(alkylthio)alkenes.[130, 144–146] The reaction is carried out without a solvent or in benzene, acetone or toluene. The reaction rate depends on the nature of ligands in the complex. Especially high activity was found for $Ni(acac)_2(PMe_2Ph)$. The catalyst activity in this reaction depends on the reactant ratio, in particular, at 100 °C and t = 2 h, the yield of bis(alkylthio)alkenes formed under catalysis by the nickel complex is 54%–87% for a disulfide to alkyne ratio of 1 : 1, while when this ratio is 1 : 3, the yields are 70%–95%. A similar complex $Pd(acac)_2(PCy_2Ph)$ (Cy is cyclohexyl) is less active but its use results in lower amounts of by-products, in particular, polymers.

A detailed investigation [130] provided the conclusion that the thioalkylation products are formed *via* the steps of oxidative addition of dialkyl disulfide to the metal (*1*), alkyne coordination to give the π-complex (*2*), insertion of the coordinated alkyne into the M–C bond (*3*) and reductive elimination of the product (*4*) (Scheme 16).

Scheme 16

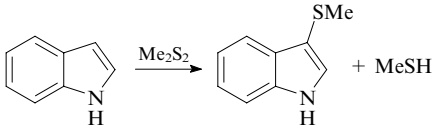


The reaction of di-n-butyl disulfide with *o*-(alk-1-ynyl)-benzoate in the presence of $FeCl_3$ in dichloroethane at 80–100 °C and t = 20–24 h results in (butylthio)-substituted isocoumarins in 82% yield.[147] In the presence of $GaCl_3$, dibutyl disulfides add to oct-1-yne.[148] In benzene at room temperature (t = 12 h), the yield of bis(alkylthio)alkene from di-n-butyl disulfide is 49%–63%; from di-*sec*-butyl disulfide and t = 20 h, the yield is 49%; in the case of phenyloctyne and dibutyl disulfide, the yield of thioalkene is 50%; and di-*tert*-butyl disulfide does not react.

2. Thioalkylation of heterocyclic compounds

The catalytic thioalkylation of heterocyclic compounds with dialkyl disulfides is performed in the liquid phase. The reaction of dialkyl disulfides with indoles occurs as thioalkylation giving (alkylthio)indole (Scheme 17).

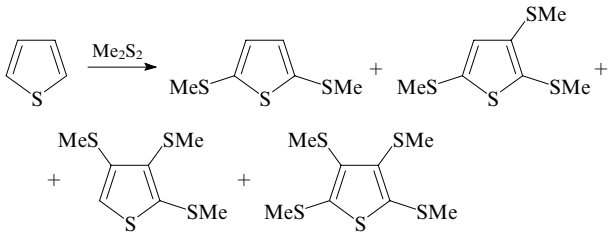
Scheme 17



In the presence of the CuI catalyst in a nitrogen atmosphere at 136–160 °C over a period of 3 h, the yield of 3-(methylthio)indole is 41%.[149]

Catalytic thioalkylation of thiophene with dialkyl disulfides is possible. In the presence of the catalyst — Zn- or Mn-chloride-modified montmorillonite clay — thiophene reacts with dimethyl disulfide to give various derivatives (Scheme 18).[150–152]

Scheme 18



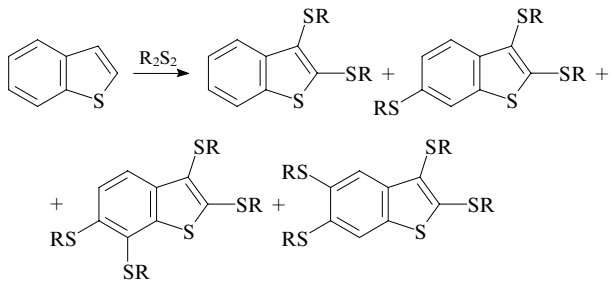
With the $ZnCl_2$/montmorillonite catalyst under argon and atmospheric pressure at 80 °C, in chlorobenzene (t = 48 h), the reaction gives predominantly the 2,3,5-

and 2,3,4-isomers in a total yield of 21% and tetrasubstituted thiophene in a 16% yield; no mono- or disubstituted thiophenes have been detected. At 150 C, elevated pressure and in the presence of air over a period of 5 h, 2,5-bis(methylthio)thiophene is formed together with tri- and tetrasubstituted derivatives. The product yield is affected by the molar ratio of the disulfide and thiophene: the higher this ratio, the lower the amount of disubstituted thiophene formed with respect to tri- and tetrasubstituted derivatives.

$Me_2S_2 : C_4H_4S$	Contents of MeS derivatives in the reaction products (mol.%)		
	2,5-$(MeS)_2$	2,3,5-$(MeS)_3$	2,3,4,5-$(MeS)_4$
0.5	33	50	18
2.0	6.6	15	78
8.0	9	12	88

The thioalkylation of benzo[*b*]thiophene with dialkyl disulfide catalyzed by $ZnCl_2$/montmorillonite affords alkylthio derivatives (Scheme 19).[150, 151]

Scheme 19



R = Alk

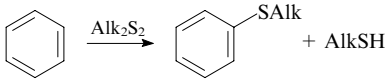
The reaction of dimethyl disulfide in dichloroethane or chlorobenzene at 130 °C at a 10-fold excess of the disulfide with respect to benzothiophene leads to the disubstituted product; no formation of the trisubstituted product is observed. When catalyzed by montmorillonite containing $MnCl_2$, the reaction also gives tetrasubstituted benzothiophene. At 80–150 °C, a stoichiometric reactant ratio and an excess of the catalyst, the reaction cannot be terminated after the formation of monosubstituted benzothiophene; only bi-, tri- and tetrtasubstituted derivatives are formed. When diethyl and di-n-propyl disulfides react with benzothiophene, the yield of disubstituted product amounts to 64%–73%; the process is substantially accelerated in the presence of air.

The mechanism of thioalkylation of thiophenes catalyzed by montmorillonite-based systems has not been studied. Non-modified montmorillonite is inactive in this reaction, and addition of the proton-donor sulfuric acid to the support only accelerates polymerization. The MCl_2/montmorillonite (M = Zn, Mn) catalyst surface bears protic and aprotic acid sites, this catalyst being active in the thioalkylation of the thiophene ring. It was assumed [150–152] that these sites are responsible for disulfide activation. Presumably, on contact with the catalyst, a surface complex is formed in which one sulfur atom of the disulfide is bonded to LAS and the second sulfur atom is linked to BAS. This induces decomposition of the disulfide at the S–S bond to give LAS-chemisorbed CH_3S fragments and the CH_3S^+ groups linked to BAS. Due to participation of lone electrons of sulfur in the aromatic conjugation, the thiophene carbon atoms are enriched in electrons, which makes possible the reaction with the surface CH_3S^+ fragments to give alkylthio derivatives of thiophene or benzothiophene. It cannot be ruled out, however, that the acid sites of the catalyst also participate in the activation of the thiophene ring. Under the action of BAS present in the catalyst, alkanethiol is also formed; in the presence of air it is oxidized to disulfide, which results in liberation of the BAS.

3. Thioalkylation of aromatic hydrocarbons and their derivatives

According to a patent,[153] the reaction of dialkyl disulfides with aromatic hydrocarbons can be induced by Al, Zn, Fe, B and Sn halides. With these compounds, the reaction of dialkyl disulfides with benzene at 82 °C proceeds as electrophilic substitution in the benzene ring and gives (alkylthio)benzene (Scheme 20).

Scheme 20



The reaction rate depends on the catalyst to disulfide molar ratio. When the disulfide to benzene ratio is < 1 and $t = 6$ h, the conversion of benzene is 8%, the selectivity of formation of (methylthio)benzene is 20%; polysulfides (0.8%–4.9% yield) and high-molecular-weight compounds (0.1%–2.9% yield) are also formed. The catalyst to disulfide ratio is important; when it is increased, the conversion increases to 65% and the selectivity increases to 56%, while the amount of by-products formed somewhat decreases; only at a twofold molar excess of the catalyst with respect to the disulfide over a period of 5 min to 1 h, the conversion is 72%–95% and the selectivity to (methylthio)benzene is 94%.

In the presence of the montmorillonite clay K10 modified with sulfuric acid or Zn, Mn, Cu and Fe chlorides, dimethyl disulfide reacts with aromatic hydrocarbons to give methylthio derivatives.[151] Table 9 presents the results of experiments in chlorobenzene at 130 °C ($t = 24$ h) and a

Table 9. Thiomethylation of aromatic hydrocarbons and anisole with dimethyl disulfide catalyzed by modified montmorillonite clay K10 at 130 °C.[151, 152]

Hydrocarbon	Position of MeS groups in the product	Yield (%)		
		K10/$ZnCl_2$	K10/H_2SO_4	K10/$MnCl_2$
Benzene	–	0	0	0
Toluene	2,4,5	0	11	5
o-Xylene	4,5	0	23	38
Anisole	4	46	15	66
	2,4,5	0	9	12
Naphthalene	1,4	21	0	64
1,3,5-Trimethylbenzene	2,4,6	90	0	0

10-fold molar excess of the disulfide with respect to the hydrocarbon. The reactions of all compounds, except for benzene, lead to methylthio derivatives with different degrees of substitution. A monosubstituted product is formed only in the reaction of dimethyl disulfide with anisole in the presence of catalysts containing $ZnCl_2$ or $MnCl_2$ on montmorillonite. A disubstituted derivative was obtained by the reaction of dimethyl disulfide with *o*-xylene and naphthalene, the highest yield being observed on a manganese-containing catalyst; the formation of trisubstituted products is difficult. Presumably, the reaction proceeds *via* the formation of a complex in which the metal cation (or a surface proton) is coordinated to one sulfur atom of the disulfide, while the second disulfide sulfur atom is linked to the hydrocarbon. Decomposition of this complex results in the formation of methanethiol and the thiomethylation product. In the presence of oxygen, the reaction is facilitated as some of methanethiol molecules formed in the reaction strongly bonded to the active site are oxidized to dimethyl disulfide, thus vacating the catalyst active sites.

The derivatives of aromatic hydrocarbons containing halogen atoms or aldehyde, keto and amino groups enter into the catalytic thioalkylation reaction with dialkyl disulfides.

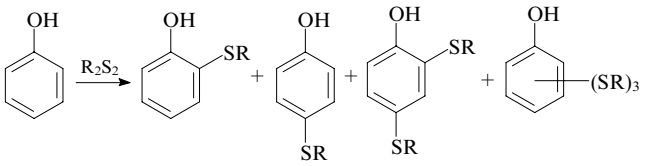
The reaction with halobenzene results in alkyl phenyl sulfide. Indeed, dimethyl disulfide reacts with iodobenzene in the presence of the Ni^{II} phosphine complex [154] in DMF (110 C, $t = 4$ h) to afford methyl phenyl sulfide in a yield of 57%–90% depending on the composition of the ligands; the reaction with chloro- and bromobenzene virtually does not take place. An efficient catalyst for the thioalkylation of iodobenzene in DMF at 110 °C is the complex $[NiCl\{(C_6H_3(OPPh_2)_2\text{-}2,6\}]$ in the presence of zinc.[155] Dialkyl disulfides R_2S_2 (R = Me, Pr^i, Bu^n, Bu^i) react with iodobenzene under the action of $NiHal_2(bipy)$ (Hal = Cl, I, Br) with addition of Zn to afford alkyl phenyl sulfides.[156] The best results were obtained for Hal = Br where the yield of the product after 48–72 h was 80% from Me_2S_2, 68% from $Pr^i_2S_2$ and 81% from $Bu^n_2S_2$; however, only traces of the sulfide were formed from $Bu^t_2S_2$. When the benzene ring has a 2- or 4-substituent (Me, MeO, H_2N, HO, Cl, Br, Ac), the product yield is 61%–92%. In the presence of copper powder as the catalyst and with subsequent treatment of the reaction mixture with Bu^nNO_2, dimethyl disulfide adds without the replacement of the halogen atom in the benzene ring containing also alkyl, alkoxy, cycloalkyl and alkenyl groups giving rise to 4-halo(alkylthio)benzenes, the yield of which reaches 89%.[157]

Dialkyl disulfides also react according to the thioalkylation pathway with aromatic hydrocarbons containing aldehyde or keto groups. In the presence of the complex $RhH(PPh_3)_4$ with 1,2-bis(diphenylphosphino)ethane, dimethyl disulfide reacts with aromatic ketones being converted to α-methylthio ketones.[158] Aromatic aldehydes, phenylacetates and phenylacetonitrile react in a similar way. Propiophenone and dimethyl disulfide react in the presence of this catalyst at reflux ($t = 3$ h) and give (methylthio)propiophenone in a yield of 91%. With the indium complex with trimethylchlorosilane as the catalyst, dimethyl disulfide in acetonitrile reacts [159] with *para*-substituted benzaldehydes containing MeO, Cl, AcO or F substituent. The reaction occurs on refluxing for 1.5–3 h and gives dithioacetals in a yield of 65%–78%.

Thioalkylation of amino-substituted benzenes is possible. Dimethyl disulfide reacts with aniline [160] in the presence of the $FeF_3–I_2$ catalyst in acetonitrile (80 °C, $t = 36$ h) to form 2- and 4-(methylthio)anilines in a 27% total yield. The reaction of diaminotoluene with dimethyl disulfide is catalyzed by ZnI_2 or by a Lewis acid (100–200 °C, $t = 1.5–2$ h).[161, 162] Active catalysts of the reaction of dimethyl disulfide with aniline [163] (unsubstituted or substituted by 2,4-Me_2, 2,6-Me_2, 4-Cl, 4-MeO and 4-NMe_2) are CuI, $AlCl_3$, $ZrCl_4$, $TiCl_4$, $FeCl_3$ and $ZnCl_2$. In a nitrogen atmosphere at 140–175 °C over a period of 15–42 h, *ortho*- and *para*-methylthio derivatives are formed with high selectivity to thioalkylation products. The reaction of dimethyl disulfide with aniline results in 2- and 4-(methylthio)anilines. The long-term reaction ($t = 120$ h) gives tri(methylthio)aniline; the highest activity was found for the CuI and $AlCl_3$ catalysts and lower activities were exhibited by $FeCl_3$ and $ZnCl_2$.

Phenols are thioalkylated under the action of various catalysts with the formation of different (alkylthio)phenols depending on the catalyst nature and reaction conditions (Scheme 21).

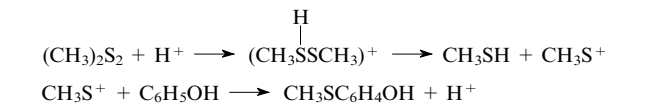
Scheme 21



R = Alk

Proton-donor catalysts are active in the thioalkylation of phenols. Patents [164, 165] and papers [166, 167] describe liquid-phase reactions of dimethyl disulfide with phenol and substituted phenols induced by phosphoric or sulfuric acid or methane- or benzenesulfonic acid. At 150–170 °C, the yield of 4-(methylthio)phenol in the presence of phosphoric acid within 16 h does not exceed 28%; in the presence of sulfuric acid within 2–6 h, 2- and 4-(alkylthio)phenols are formed in a 40%–75% yield. It was reported [167] that dimethyl disulfide reacts with phenol in concentrated sulfuric acid at 130–150 °C, $t = 4$ h to give mainly 4-(methylthio)phenol in 79%–83.5% yield. Dimethyl disulfide also reacts with mono- and disubstituted phenols $R_nC_6H_{5-n}OH$ (R_n = 3-Me, 3-Et, 3-Pr^i, 3-MeO, 2-Ph, 4-Me, 4-Cl, 3,5-Me_2, 3,5-Pr^i_2, 3-Me-6-Pr^i, 2-Me-5-Pr^i). In *para*-substituted phenol, the methylthio group adds to the *ortho*-position of the ring. Depending on the reactant structure, the yields of thioalkylation products were 30%–100%. Presumably,[166] thioalkylation of phenols catalyzed by proton-donor compounds proceeds *via* the dimethyl disulfide protonation step, resulting in S–S bond cleavage giving highly reactive CH_3S^+ ion. This ion attacks the aromatic ring, thus giving (methylthio)phenol and regenerating the proton on the surface (Scheme 22).

Scheme 22

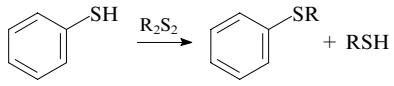


Aprotic acids can also have a catalytic effect in the thioalkylation of phenol. In the presence of a zirconium

phenoxide catalyst[168] at 150–200 °C, $t = 6–10$ h, phenol : disulfide molar ratios from 3 : 1 to 1 : 3 and catalyst : disulfide molar ratios from 0.99 : 1 to 0.01 : 1, the addition of dimethyl, diethyl and di-n-propyl disulfides to phenol produces *o*-(alkylthio)phenols in a 40% yield. Under the action of aluminium phenoxide catalyst[169] at 120–185 °C, $t = 2–5$ h, and catalyst : disulfide molar ratio of (0.01–0.2) : 1, dimethyl and diethyl disulfides react with unsubstituted phenol, 3-Et- or 4-Cl-substituted phenol or cresol to give *ortho*- and *para*-substituted phenols with the *ortho*-isomer predominating. The Lewis acids $AlCl_3$, $AlBr_3$ $ZnCl_2$, $FeCl_3$, $SnCl_4$, $AsCl_5$ or BF_3 in alkylbenzene solution at 100 °C and an excess of disulfide with respect to phenol ($t = 4–14$ h) accelerate the reaction of Me_2S_2, Et_2S_2 and $Bu^n_2S_2$ with the phenols $R_nC_6H_{5-n}OH$ (R_n = 4-Cl, 4-Bu^t, 2,4-Me_2), the reaction giving mainly *ortho*-alkylthio derivatives in a yield of up to 92%.[170–172] Amorphous and crystalline aluminosilicates are active catalysts for phenol thioalkylation.[173–176] In the gas phase at 270–400 °C, only decomposition of dialkyl disulfide takes place.

The liquid-phase reaction of phenol with dimethyl, diethyl and dipropyl disulfides in the presence of amorphous aluminosilicate and zeolites in the hydrogen form (HY and HZSM-5) has been carried out at 100–130 °C, a catalyst to dimethyl disulfide ratio from 0.2 : 1 to 0.6 : 1 and $t = 2–24$ h. At 120 °C and $t = 4$ h, monosubstituted phenols are formed as equal amounts of *ortho*- and *para*-isomers; longer reaction time (24 h) results in the *ortho*-isomer predominating. Under more rigorous conditions, for example, at 150–180 °C, $t = 30–100$ h, a mixture of *ortho*- and *para*-substituted phenols is formed. In the presence of the HZSM-5 zeolite, only monosubstituted phenol is obtained, while HY and amorphous aluminosilicate catalyze the formation of mono- and disubstituted phenols. The authors attributed this result to different porous structures of these zeolite types. However, it is more likely that this outcome is due to different surface acidities of the catalysts used. In the presence of zeolites, thioalkylation of benzenethiol with disulfides does not take place; instead, the disulfide adds to the thiol sulfur atom with subsequent decomposition and generation of alkanethiol and alkyl phenyl sulfide (Scheme 23).

Scheme 23



A detailed investigation of the thioalkylation of phenol with dialkyl disulfides has been reported.[49, 175] It was found that the reaction rate and selectivities of formation of thioalkylation products depend on the zeolite composition, acidity of its surface and reaction conditions. In all cases, 2- or 4-(methylthio)phenol is first formed with the *para*-isomer predominating. The ratio of the monosubstituted isomeric phenols and the yields of by-products vary depending on the zeolite composition, reactant concentrations and reaction time. When dimethyl disulfide is taken in a sixfold excess with respect to phenol ($t = 24$ h), the highest activity is observed for dealuminated HY zeolite (Si : Al = 20) with enhanced protic acidity. This catalyst provides the formation of mono- and disubstituted phenols; the *ortho* to *para* ratio for monosubstituted isomers is low. The HY zeolite (Si : Al = 2.5) is less active but more selective in the formation of monosubstituted (alkylthio)phenol: for 47% conversion of the disulfide, the selectivity is 96% but at Si : Al = 20% and 97% conversion of the disulfide, the selectivity decreases to 56%. As the disulfide conversion increases, the *ortho* to *para* ratio for monosubstituted isomers becomes higher. Less active zeolites are more selective towards the formation of mono(alkylthio) derivatives, the *para*-isomer being formed predominantly. When more active zeolites are used, more disubstituted phenols are formed.

The kinetic measurements show that in the case of reaction with approximately equal reactant concentrations, *ortho* derivative is the major product. When phenol is taken in excess with respect to dimethyl disulfide, the thioalkylation rate decreases, *para*-isomer predominates and large amounts of disubstituted phenols are produced. When an excess of dimethyl disulfide is used, the major product is 2,4-di(methylthio)phenol. The mechanism of the first step — the formation of monosubstituted phenol in the presence of HY zeolite with Si : Al = 20 — was established from kinetic and adsorption data.[49, 175] A study of the effect of the reaction time on the product ratio at 110 °C demonstrated that in the beginning of the process, 4-(methylthio)-phenol is mainly formed; after 15 min from the onset of the reaction, the isomer ratio *ortho* : *para* = 38 : 62, but as the experiment duration increases to 8 h, this ratio becomes 68 : 32 for a 90% conversion of phenol, and disubstituted phenols are also formed. When the starting concentrations of the reactants vary, the isomers are formed in different ratios (Table 10). At a high excess of phenol with respect to disulfide, the *para*-isomer is the major reaction product; at lower phenol contents, the amount of this isomer decreases and the yield of the *ortho*-isomer increases. When a very high excess of disulfide with respect to phenol is used, disubstituted phenol becomes the major reaction product, while the formation of *ortho*- and especially *para*-isomers substantially diminishes. This result was attributed[49, 175] to different adsorption capacities of reactants on the zeolite surface, which was confirmed by IR-spectroscopy study of the reactant adsorption. The following reaction mechanism was postulated. On contact of phenol with zeolite, the oxygen atom of the phenolic OH group interacts with the protic site of the catalyst, while the benzene ring does not participate in adsorption. The coordination of dimethyl disulfide to the protic site involving one sulfur atom induces cleavage of the disulfide S–S bond to give methanethiol and the CH_3S^+ group stabilized on the oxygen atom of the zeolite hydroxyl group. The reaction of surface CH_3S^+ groups with protonated phenol gives rise to (methylthio)-phenols.

Table 10. Effect of phenol to dimethyl disulfide ratio on the distribution of phenol thiomethylation products at 110 °C.[149, 175]

Phenol : dimethyl disulfide (mol.)	Relative content in phenol thiomethylation products (%)			
	monosubstituted		disubsti-tuted	trisubs-tituted
	para	*ortho*		
15	70	28	2	0
4	14	83	3	0
3.3	12	43	42	0
1.1	4	23	60	13

4. Thioalkylation of alkanols

Under the action of heterogeneous catalysts, dimethyl disulfide can react with methanol. For example, in the presence of alumina in an inert atmosphere at elevated temperature, the reaction of dimethyl disulfide with methanol results in the formation of sulfur-containing products: dimethyl sulfide, methanethiol and hydrogen sulfide.[176, 177] In the presence of a catalyst and at a short contact time, pure methanol is only dehydrated to dimethyl ether; at longer contact times, carbon oxides are also detected in the reaction products. For a mixture of methanol with dimethyl disulfide at a short contact time, the yield of dimethyl ether approximately corresponds to the conversion of methanol, as upon the dehydration of pure methanol, but at longer contact times, the yield of dimethyl ether sharply decreases, the yields of carbon oxides somewhat increase and dimethyl sulfide is also formed, its yield in relation to starting dimethyl disulfide being 2 times higher than the disulfide conversion (Fig. 6). The yield of dimethyl sulfide increases following an increase in the methanol : disulfide molar ratio. The following results were obtained at 350 °C on γ-Al_2O_3 for a 70% conversion of the disulfide:

$MeOH : Me_2S_2$	0.2	0.6	1.2	1.7	2.0	2.4	2.6
Yield of Me_2S (mol.%)	60	76	106	118	126	134	136

Methanol mainly reacts with disulfide to afford dimethyl sulfide but some methanol (15%–25%) decomposes to give dimethyl ether and carbon oxides. The highest yield of dimethyl sulfide is formed when $MeOH : Me_2S_2 \geqslant 2$. The concentration of methanol that has reacted with the disulfide (the difference between the methanol concentration in the initial reaction mixture and the sum of concentrations of the unchanged methanol and formed dimethyl ether and carbon oxides) for most of the catalysts coincides within the experimental error with the concentration of the dimethyl sulfide formed. This result provides the conclusion[176, 177] that the reaction shown below occurrs in a dimethyl disulfide and methanol mixture (Scheme 24).

Scheme 24

$$(CH_3)_2S_2 + 2\,CH_3OH \xrightarrow{[H^+]} 2\,(CH_3)_2S + 2\,H_2O$$

This process involves the protons contained in the catalyst; they are continuously reproduced on the surface *via* methanol decomposition.

The activity of catalysts in the formation of dimethyl sulfide from dimethyl disulfide and methanol depends on the type, strength and concentration of the acidic and basic sites on their surface[178–180] (see Table 2). The activities of various catalysts in the reaction of dimethyl disulfide with methanol have been compared [the rate of formation of dimethyl sulfide in mmol h^{-1} (g cat)$^{-1}$ at 350 °C, a methanol to disulfide molar ratio of 2.5 and a 70% conversion of dimethyl disulfide served as the measure of activity] (Table 11). The trends of variation of the catalyst activity as a function of acid-base characteristics of the surface proved to be the same as in the conversion of pure dimethyl disulfide under inert atmosphere. The catalysts with high contents of alkaline additives (Na/Al_2O_3, K_2WO_4/SiO_2 and K_2W_4/Al_2O_3) have no BAS but have weak LAS and strong BS. In the presence of such catalysts, the yield of dimethyl sulfide is 5%–10%, the major reaction product is methanethiol. The surface of NaX zeolite also bears no BAS and has weak LAS and medium-strength BS. The dimethyl disulfide conversion with this catalyst gives mainly meth-

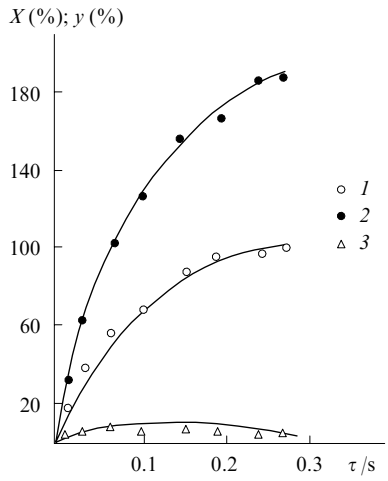


Figure 6. Conversion of dimethyl disulfide [*X* (%)] during transformation in a mixture with methanol (*1*) and yields [*y* (mol.%)] of dimethyl sulfide (*2*) and methanethiol (*3*) *vs.* contact time (the catalyst is Cr/α-Al_2O_3, 350 °C).[178]

Table 11. Catalyst activity in the reaction of dimethyl disulfide and methanol to give dimethyl sulfide and in the reaction of formation of dimethyl ether upon methanol dehydration.[178]

Catalyst	Yield (mol.%)		Formation rate /mmol h^{-1} (g cat)$^{-1}$	
	Me_2S	MeSH	Me_2S	Me_2O
Zeolites, supported acids and bases				
1.7% Na/γ-Al_2O_3	9.8	82	0.15	2.1
K_2WO_4/SiO_2	5.6	63	0.08	0.13
K_2WO_4/γ-Al_2O_3	7.0	65	0.16	0.15
NaX	28	55	6.4	0.60
H_3PO_4/SiO_2	0	43	0	0.21
$HiSiW/SiO_2$	132	3.5	5.0	14.8
HNaY	112	14	24.8	36.3
HZSM-5	126	4.2	32.4	92.7
CoHZSM-5	118	8.4	37.4	29.5
Oxide catalysts				
Cr/SiO_2	24	5.2	1.6	3.3
γ-Al_2O_3	134	0.7	3.6	68
0.2% Na/γ-Al_2O_3	133	2.8	2.0	61
H_2SO_4/γ-Al_2O_3	126	4.9	5.7	113
W/Al_2O_3	136	1.4	11.2	68
Co/γ-Al_2O_3	95	18.9	28.6	32
Mo/γ-Al_2O_3	112	12.6	37.2	42
Cr/γ-Al_2O_3	130	4.2	49.6	54
Ni,Mo/γ-Al_2O_3	91	21	16.0	38

Note. $T = 350$ °C; the methanol : dimethyl disulfide molar ratio is 2.4–2.6; the conversion of dimethyl disulfide is 70%, that of methanol is 50%.

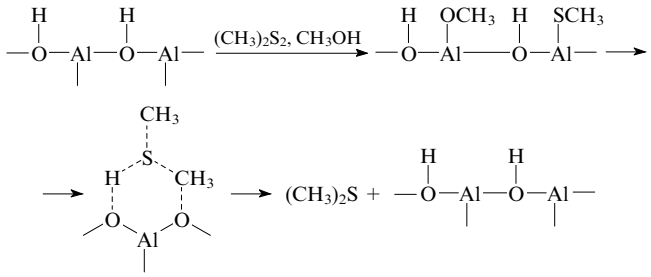
anethiol; the yield of dimethyl sulfide is <30 mol.%, formation rate being higher than that observed in the presence of supported alkaline catalysts.

The H_3PO_4/SiO_2 catalyst containing only weak BAS and weak BS is absolutely inactive. The $HSiW/SiO_2$ catalyst surface has no LAS but has strong BAS and weak BS. This catalyst has a noticeable activity towards the formation of dimethyl sulfide. The hydrogen forms of HNaY and HZSM-5 zeolites containing strong BAS and strong LAS and also medium-strength BS show a high activity towards dimethyl sulfide formation. After the introduction of 2.5 mass % of cobalt into HZSM-5 zeolite, the Lewis acidity of the surface increases and strong BAS are also present on the catalyst surface; however, the activity of this catalyst resembles that of pure zeolite. The activity of γ-Al_2O_3 having mainly strong LAS and medium-strength BS is of the same order as that of $HSiW/SiO_2$. After treatment of γ-Al_2O_3 with an $H_2S + H_2$ mixture at 400 °C, some strong BAS appear on the surface, and the activity of this catalyst increases 1.4-fold compared with pure γ-Al_2O_3. The introduction of 0.2 mass % of Na into γ-Al_2O_3 markedly suppresses BAS, decreases the strength of LAS and somewhat increases the surface basicity. As compared with non-modified γ-Al_2O_3, the reaction rate reduces 1.8-fold. The addition of sulfuric acid to γ-Al_2O_3 increases the concentration of strong BAS, enhances the strength of LAS, and the catalyst activity increases 1.6-fold; the insufficiently high activity is due to blocking of BS by sulfuric acid. Upon introduction of transition metal oxides into γ-Al_2O_3, strong BAS appear on the surface, and fairly large numbers of strong LAS and medium-strength BS are also present. These catalysts are close in activity to hydrogen forms of zeolites and surpass non-modified aluminium oxide.

When silica is used as the support, the activity of oxide catalysts decreases. The Cr/SiO_2 catalyst having strong BAS, reduced-strength LAS and weak BS on the surface has lower activity than the alumina–chromium catalyst. Thus, if the catalyst surface bears only weak protic sites, no dimethyl sulfide is formed from dimethyl disulfide and methanol. Catalysts with strong BS and weak LAS containing no BAS show low activity in this reaction; the decrease in the BS strength entails some increase in the activity. The catalyst having medium-strength BS and only strong BAS or only LAS show moderate activity. For the formation of dimethyl sulfide, most efficient are catalysts the surface of which bears simultaneously medium-strength BS, strong BAS and strong LAS, in particular, γ-Al_2O_3-supported chromium oxide. In the presence of this catalyst at 350–400 °C, the selectivity of formation of dimethyl sulfide is 95%–98%.

The acid-base properties of the catalyst surface affect also the rate of methoxylation of the surface in the reaction with pure methanol. The trends of variation of the methoxylation rate with methanol depending on the catalyst composition are qualitatively the same as for the formation of dimethyl sulfide. Presumably, both reactions are performed by the same surface sites. A quantitative correlation is unsatisfactory. This may be due to the fact that the rate of surface methoxylation with methanol is not the rate-limiting step in the synthesis of dimethyl sulfide. The dehydration of methanol[68,181] occurs *via* surface methoxylation followed by the formation of the surface complex comprising one CH_3O group and gaseous methanol or the second CH_3O group. In this complex, the oxygen atom of one CH_3O group is linked to LAS, while that of the other CH_3O group is linked to the BAS on the surface. In the case of dimethyl disulfide conversion in a mixture with methanol, the formation of dimethyl sulfide occurs *via* a similar surface complex but comprising bonds between the acid-base sites and CH_3O and CH_3S groups arising from methanol and dimethyl disulfide (Scheme 25).

Scheme 25



Most likely is the formation of such complexes for catalysts that contain simultaneously strong protic and strong aprotic acid sites and medium-strength basic sites on the surface, in particular, for zeolite hydrogen forms and transition metal oxides supported on γ-Al_2O_3. In the presence of methanol, the coordination of the disulfide CH_3S groups to the LAS and BS is difficult and the disulfide C–S bond cleavage, resulting in the formation of by-products, is ruled out. As a result, the process is highly selective to dimethyl sulfide.

Characteristics of the process of conversion of dimethyl disulfide in a mixture with methanol vary depending on the content of the active component in the catalyst.[179,180] For example, it was found for Cr/Al_2O_3 that catalysts containing up to 3 mass % Cr provide the formation of low yields of methanethiol (2 mol.%–5 mol.%) but the yield increases with an increase in the chromium content in the catalyst to reach 60% on a bulk sample. The introduction of 0.12 mass % Cr into γ-Al_2O_3 leads to an increase in the rate of transformation of dimethyl disulfide 2.6-fold; on further increase in the chromium content it also increases, and for 10% Cr/Al_2O_3 it is 17 times higher than the value observed for pure alumina. The increase in the catalyst activity in the formation of dimethyl sulfide with an increase in the Cr content is due to the enhancement of the protic acidity of the surface with respect to the pure support. It follows from kinetic measurements that in the presence of alumina–chromium catalysts, the reaction rate is directly proportional to the concentrations of both methanol and disulfide. At higher temperature, the reaction rate increases, and the apparent activation energy is 67 ± 2 kJ mol^{-1}. At 350–400 °C, a methanol to disulfide molar ratio of >2 and 100% conversion of reactants, almost complete conversion of dimethyl disulfide to dimethyl sulfide can be attained, the yields of sulfur-containing by-products being insignificant.

VII. Conclusion

The research into the catalytic reactions of dialkyl disulfides has been started rather recently; nevertheless, numerous works have been carried out in this field, indicating that dialkyl disulfides can serve for targeted catalytic syntheses of diverse organic compounds of sulfur. The syntheses consist of one step and most often afford alkylthio deriva-

tives in high yields and with rather high selectivity. Analysis of the presented information attests to good prospects of using dialkyl disulfides in the catalytic syntheses of various valuable products.

The selection of active catalysts and determination of conditions of some selective processes such as the preparation of alkanethiols, dialkyl sulfides and thiophene were preceded by detailed investigations of the nature of the catalyst active sites, mechanism of action and reaction kinetics. This gave the results that may provide the basis for the development of new synthetic methods. For other transformation processes of lower dialkyl disulfides, detailed investigations have not been carried out and the proposed catalysts and conditions of syntheses cannot be regarded as optimal. It is important that the possibility of one-sep processes for the synthesis of desired thio compounds in preparative yields under the action of some catalysts has been ascertained. However, in most cases, long reaction times are needed to achieve high yields, and mixtures of isomers are often formed in the reactions. Moreover, processes were carried out in the liquid phase and there are some technological problems related to the difficulty of isolation of reaction products and the catalyst from the reaction mixture and to waste disposal.

It is more promising to carry out heterogeneous catalyzed reactions in the gas phase but the number of such studies is insufficient. In the syntheses of particular thio compounds with the proposed catalysts, researchers obtained dissimilar results and, since the reactions have been carried out under non-commensurable conditions, the results cannot be integrated and it is difficult to draw conclusions about the advantages of one or another catalytic system. The problem of development of effective catalysts for these processes and elucidation of the optimal reaction conditions has not been completely solved as yet. Studies in this field should be continued in order to elucidate the detailed mechanism and kinetics of known reactions, to find more effective catalytic systems, to determine the effect of the catalyst composition and preparation procedure on the activity, selectivity and stability. In addition, it is desirable to continue the search for new catalytic systems for the synthesis of various valuable compounds of sulfur based on transformation of lower dialkyl disulfides. The results of fundamental research will be useful both for the design of new catalyzed syntheses based on dialkyl disulfides and for the development of the whole scientific area on catalysis of reactions of organic sulfur compounds.

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