

# Catalytic Conversions of Dialkyl Disulfides

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**Abstract**—The results of the studies of catalytic conversions of lower dialkyl disulfides performed at the Boreskov Institute of Catalysis (Siberian Branch, Russian Academy of Sciences) are summarized. The selective hydrogenolysis of dimethyl and diethyl disulfides with the formation of alkanethiols occurs in a hydrogen medium on transition metal sulfides. Dimethyl disulfide turns into dimethyl sulfide in an inert gas medium on oxide catalysts with acid and basic sites on their surface. Lower dialkyl disulfides are dehydrocyclized to thiophene under the action of sulfide catalysts. In an oxygen medium on the metal oxides and salts, diethyl disulfide and a lower disulfide concentrate are selectively oxidized to form alkanethiol sulfonates, alkanethiol sulfonates, and alkanesulfonic acids.

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## INTRODUCTION

Hydrocarbon gases from some gas-condensate and petroleum fields contain lower alkanethiols. The oxidative purification of these gases produces large quantities of a mixture of lower dialkyl disulfides,  $C_1-C_4$ , which presently find only limited use. The major amount of disulfides is subjected to incineration, which produces atmospheric pollutants. At the same time, the lower disulfides can be converted into valuable thio compounds, such as alkanethiols, dialkyl sulfides, thiophenes, sulfonates, sulfonates, and sulfonic acids, which can find practical use [1–3]. For example, methanethiol is used in the synthesis of methionine (medicine and component of poultry feed and fodder). Alkanethiols with  $C_2-C_4$  radicals are odorants for fuel gases and are employed in the synthesis of agricultural chemicals, household chemicals, and surfactants. Dialkyl sulfides can be used as extracting agents for noble metals, flotation agents, odorants, and starting compounds in the synthesis of various valuable substances. For instance, dimethyl sulfoxide (medicine and solvent) is synthesized from dimethyl sulfide. Thiophene is used in the synthesis of physiologically active substances, dyes, oil additives, and polyorganosiloxanes. Thiolsulfonates and thiolsulfonates are bactericides and anti-inflammatory agents, and lower alkanesulfonic acids are efficient acid-type catalysts for a number of important reactions.

The possibility of various conversions of dialkyl disulfides is due to their specific properties [4]. The sulfur atoms in disulfides have lone electron pairs capable of participating in complex formation. This activates the sulfur atom so that it gains the capability for reacting with nucleophilic agents. The S–S bond in dialkyl disulfides is unstable and is readily cleaved under mild conditions to form alkanethio groups, which can

undergo various conversions. Catalytic methods are especially promising for the conversion of dialkyl disulfides into valuable thio compounds. Studies in this area have been performed over several years at the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences.

Here, we review the studies of the decomposition of lower dialkyl disulfides to alkanethiols and dialkyl sulfides and their cyclization into thiophene and partial oxidation.

## SYNTHESIS OF ALKANETHIOLS

The decomposition of dimethyl and diethyl disulfides at  $T = 190$ – $350^\circ\text{C}$  in a helium atmosphere on oxide catalysts (aluminum, silicon, and molybdenum oxides, zeolites, and others) affords methane- and ethanethiols and by-products [5–8]. The conversion of dialkyl disulfides (X, %) and the yield of products (y, mol %) increase with an increase in the temperature and contact time ( $\tau$ ). At lower temperatures and short  $\tau$ , thiol and cracking products formed in parallel directly from the disulfide. At elevated temperatures and longer contact times, alkanethiols are converted into dialkyl sulfides and  $\text{H}_2\text{S}$ . The resulting thiol and sulfide decompose partially into hydrogen sulfide, sulfur, and hydrocarbons. The acidic properties of the surface affect the activity of the oxide catalysts in the formation of alkanethiols from dialkyl disulfides. For instance,  $\text{SiO}_2$  contains only very weak protonic sites, and, in the presence of  $\text{SiO}_2$ , the thiol forms at a very low rate. The rate of this reaction on zeolite HZSM-5, which has strong protonic sites, is higher by a factor of ~60 times than that on  $\text{SiO}_2$ . The high rate of alkanethiol (AT) formation is observed in the presence of catalysts with Lewis acid sites (L sites) on the surface, and the weaker

**Table 1.** Activity of oxide catalysts and methanethiol selectivity in dimethyl disulfide conversion in various media at  $T = 350^\circ\text{C}$  and  $X = 90\%$ 

Catalyst	In dry helium		In helium containing 6 vol % $\text{H}_2\text{O}$		In helium containing 9 vol % $\text{H}_2\text{S}$	
	$w$ , $\text{mmol h}^{-1} (\text{g Cat})^{-1}$	$S$ , %	$w$ , $\text{mmol h}^{-1} (\text{g Cat})^{-1}$	$S$ , %	$w$ , $\text{mmol h}^{-1} (\text{g Cat})^{-1}$	$S$ , %
HZSM-5	18	7	16	24	27	51
$\gamma\text{-Al}_2\text{O}_3$	20	11	8	53	146	78
$\text{Mo}/\text{Al}_2\text{O}_3$	37	15	22	67	140	77
$\text{K}_2\text{WO}_4/\text{Al}_2\text{O}_3$	17	60	24	78	41	71
$\text{K}/\text{SiO}_2$	18	76	12	84	52	80
NaX	31	64	29	80	192	67
Na/ $\text{Al}_2\text{O}_3$	36	60	33	87	168	76

these L sites, the higher the thiol selectivity ( $S_{\text{AT}}$ ). For example, the  $\gamma\text{-Al}_2\text{O}_3$  surface contains L sites for which the heat of adsorption of CO ( $Q_{\text{CO}}$ ) is 34 kJ/mol and a small number of sites with  $Q_{\text{CO}} = 41$  kJ/mol. The selectivity of methanethiol (MT) formation ( $S_{\text{MT}}$ ) from dimethyl disulfide on this catalyst at  $T = 190^\circ\text{C}$  is 20%. After 0.023, 0.23, and 2.3 wt % sodium oxide was introduced into  $\gamma\text{-Al}_2\text{O}_3$ , the strength of the L sites decreased ( $Q_{\text{CO}} = 31$ , 27, and 18 kJ/mol, respectively) and  $S_{\text{MT}}$  increased to 30, 70, and 85%, respectively. Some increase in  $S_{\text{AT}}$  on the oxide catalysts occurs when water or hydrogen sulfide is introduced into the reaction medium [6, 7] (Table 1). The maximum  $S_{\text{MT}}$  values achieved for dimethyl disulfide conversion were 76 (with  $\text{H}_2\text{O}$ ) and 87% (with  $\text{H}_2\text{S}$ ). Disadvantages of the oxide catalysts are their deactivation during the reaction, a low alkanethiol selectivity, and the formation of considerable amounts of cracking products.

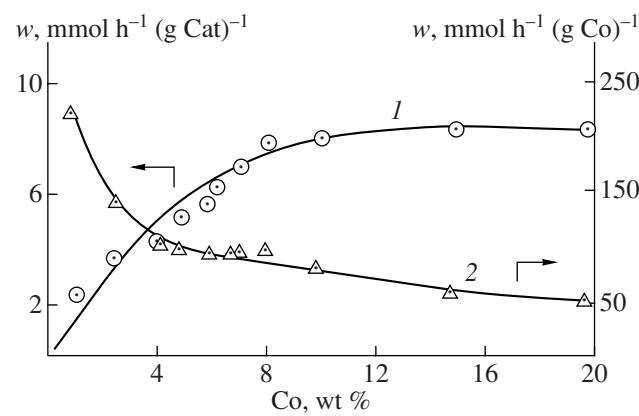
The best results were obtained for dialkyl disulfide conversion in a hydrogen medium on transition metal sulfides at  $T = 180\text{--}260^\circ\text{C}$  [9–13], when selective hydrogenolysis occurred:



At  $T \leq 200^\circ\text{C}$  and a low disulfide conversion,  $S_{\text{AT}} \geq 97\%$  and the yield of by-products (dialkyl sulfides) is 0.1–3.0 mol %; under more severe conditions, the yield of by-products is somewhat higher. The conversion value exerts no effect on the alkanethiol selectivity. At  $T = 250^\circ\text{C}$ , a high  $S_{\text{AT}}$  is observed only at a very low conversion of the initial disulfide. At  $T = 350^\circ\text{C}$ , most of the dialkyl disulfide undergoes deep hydrogenolysis with the C–S bond cleavage and  $\text{H}_2\text{S}$ , and hydrocarbon formation and the thiol selectivity  $S_{\text{AT}}$  does not exceed 5%. At a low hydrogen content of the reaction mixture ( $\text{H}_2/(\text{CH}_3)_2\text{S}_2 = 2 : 1$ ), dimethyl disulfide hydrogenolysis on the sulfide catalysts at  $T = 200^\circ\text{C}$  occurs at a low rate and is nonselective, and  $S_{\text{MT}}$  increases upon the addition of water or  $\text{H}_2\text{S}$  to the reaction mixture [14, 15]. The study of the hydrogenolysis kinetics on the  $\text{Rh}/\text{Al}_2\text{O}_3$  sulfide catalyst at  $T = 200^\circ\text{C}$  shows that, at

$[(\text{CH}_3)_2\text{S}_2]_0 \leq 2$  vol % and  $[\text{H}_2]_0 \leq 15$  vol %, the reaction is first-order and, at higher reactant concentrations, the reaction order is zero. The rate of dimethyl disulfide hydrogenolysis increases ( $E_{\text{app}} = 46 \pm 4$  kJ/mol) as the temperature is raised.

The activity of the supported sulfide catalysts in disulfide hydrogenolysis depends on the support nature (Table 2). Metal sulfides supported on  $\text{Al}_2\text{O}_3$  possess the highest activity at  $T = 200^\circ\text{C}$ , whereas, among the catalysts based on  $\text{Al}_2\text{O}_3$ , the rhodium and cobalt systems are the most efficient. For the sulfide cobalt catalysts [11], as the supported cobalt content of  $\text{Al}_2\text{O}_3$  is increased from 1 to 8 wt %, the methanethiol formation rate per gram of the catalyst increases to some limit and then remains unchanged and the rate per gram of Co decreases, probably due to the decrease in the degree of dispersion of Co (Fig. 1). As the cobalt content of the catalyst increases, the yield of the by-product (dimethyl sulfide) decreases; for example, for 2.5 and 10% Co supported on  $\text{Al}_2\text{O}_3$ , the dimethyl sulfide yield is 2.5 and 0.3 mol %, respectively.

**Fig. 1.** Influence of the percentage of cobalt on  $\text{Al}_2\text{O}_3$  on the rate of methanethiol formation from dimethyl disulfide (1) per gram of catalyst and (2) per gram of cobalt ( $X = 60\%$ ).

**Table 2.** Influence of the support nature on the activity of sulfide catalysts in the hydrogenolysis of dimethyl and diethyl disulfides into thiols at  $T = 200^\circ\text{C}$  and  $X = 50\%$ 

Metal sulfide*	Reaction rate, $\text{mmol h}^{-1} (\text{g M})^{-1}$					
	$\text{Al}_2\text{O}_3$		carbon support		$\text{SiO}_2$	
	$(\text{CH}_3)_2\text{S}_2$	$(\text{C}_2\text{H}_5)_2\text{S}_2$	$(\text{CH}_3)_2\text{S}_2$	$(\text{C}_2\text{H}_5)_2\text{S}_2$	$(\text{CH}_3)_2\text{S}_2$	$(\text{C}_2\text{H}_5)_2\text{S}_2$
Rh	217	195	200	155	164	169
Co	116	288	65	215	69	83
Ru	76	127	69	76	37	75
Mo	69	122	16	22	18	15
Ni	55	120	30	63	30	29
Pd	23	123	22	14	8	20
W	8	23	10	8	4	18

\* Metal content of the catalyst, wt %: Mo, 10; W, 18; other metals, 5.

The activity of the cobalt sulfide catalysts depends on the temperature of their treatment with a 15%  $\text{H}_2\text{S}$  + 85%  $\text{H}_2$  mixture. The reaction rate increases by a factor of 1.5 as the temperature is increased from 200 to  $400^\circ\text{C}$ . However, sulfidation at a higher temperature reduces the catalytic activity. As a result of sulfidation at  $T = 200\text{--}400^\circ\text{C}$ , the catalyst loses some amount of sulfur to form coordinately unsaturated Co cations [16], which are likely involved in disulfide activation. After the catalyst was treated at  $T > 400^\circ\text{C}$ , the concentration of coordinately unsaturated cations on the surface increased. This probably favors the hydrogenolysis of dimethyl sulfide to methanethiol and also the side condensation reaction due to which  $S_{\text{MT}}$  decreases. The specific surface area, phase composition, and structure of  $\text{Al}_2\text{O}_3$  exert no appreciable effect on the specific activity of the Co catalysts. The activity of the cobalt sulfide catalysts depends on the nature of the active component precursor and on the conditions of their thermal treatment before sulfidation. The catalysts based on cobalt acetate are  $\sim 1.4$  times more active than the catalysts obtained from cobalt chloride or nitrate. The method of Co-precursor supporting has a great effect. The 10% Co/ $\text{Al}_2\text{O}_3$  catalyst obtained using cobalt nitrate followed by its conversion on the surface into cobalt hydroxide (containing Co nanoparticles 1.5–2.0 nm in size) is  $\sim 2$  times more active than the catalysts based on the salts with a Co particle size of 30–40 nm [13].

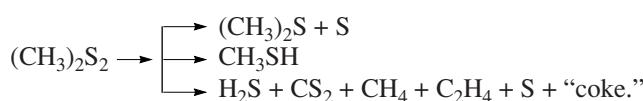
The hydrogenolysis of dialkyl disulfides at the S–S bond also occurs under the action of the bimetallic sulfide catalysts Ni(Co),Mo/ $\text{Al}_2\text{O}_3$ . In their presence at  $T \leq 200^\circ\text{C}$ , dimethyl and diethyl disulfides decompose to thiols, whose yield is as high as 95–100 mol % [9, 12]. The activity of the bimetallic sulfide catalysts depends on the nature of the precursor of the active substance. For instance, the catalysts based on phosphomolybdc acid and nickel nitrate are 1.4–2.6 times more active

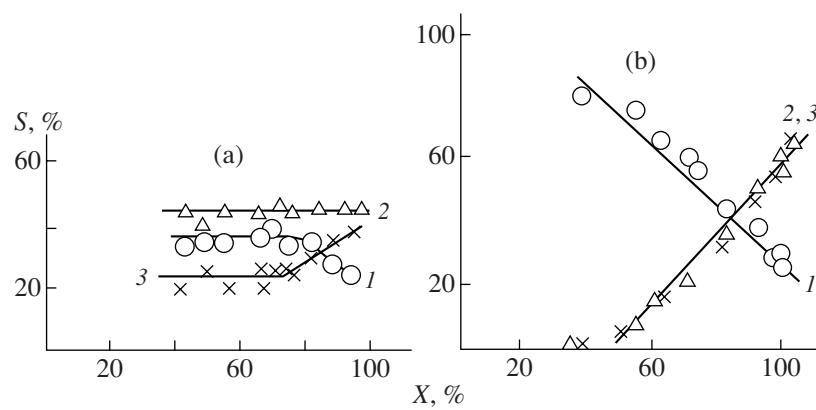
than the catalysts obtained from ammonium heptamolybdate and (Ni,Co) nitrate or chloride. The AlNiMo catalysts are  $\sim 2$  times more active than AlCoMo. The activity of the bimetallic catalysts in disulfide hydrogenolysis to thiol depends on the atomic ratio of the metals. For example, the highest activity in dimethyl disulfide hydrogenolysis on AlNiMo is achieved at  $\text{Ni}/(\text{Ni} + \text{Mo}) = 0.2\text{--}0.3$ . The highest activity per gram of the catalyst at  $T = 190^\circ\text{C}$  is observed for the alumina-supported catalysts containing 2.5–5 wt % Ni and 10–12 wt % Mo. The atomic activity of the bimetallic sulfide catalysts Ni(Co),Mo/ $\text{Al}_2\text{O}_3$  in dimethyl disulfide hydrogenolysis at the S–S bond is equal to, or lower than, the total activity of the monometallic catalysts. The activity of the Ni,Mo/ $\text{Al}_2\text{O}_3$  sulfide catalysts in methanethiol formation from dimethyl disulfide is similar to that of Rh and Co sulfides supported on  $\text{Al}_2\text{O}_3$ .

The above data suggest that, in order to obtain alkanethiols from dialkyl disulfides with a high efficiency and a high  $S_{\text{AT}}$ , the synthesis should be performed in a hydrogen medium in the presence of a sulfide catalyst.

## SYNTHESIS OF DIMETHYL SULFIDE

In the presence of catalysts containing acid and basic sites at atmospheric pressure and  $T = 190\text{--}350^\circ\text{C}$  in a helium medium, dimethyl disulfide decomposes to dimethyl sulfide, methanethiol,  $\text{H}_2\text{S}$ ,  $\text{CS}_2$ , and  $\text{C}_1\text{--}\text{C}_2$  hydrocarbons [5–8]. As follows from the dependence of the selectivity on the disulfide conversion on zeolite HZSM-5 (Fig. 2), at a low temperature the reaction products are formed in parallel directly from the disulfide:





**Fig. 2.** Selectivity with respect to (1) methanethiol, (2) dimethyl sulfide, and (3) H<sub>2</sub>S at different values of the dimethyl disulfide conversion in the presence of zeolite HZSM-5 at  $T =$  (a) 190°C and (b) 330°C.

At elevated temperatures, dimethyl sulfide (DMS) forms mainly by the condensation of the resulting methanethiol:

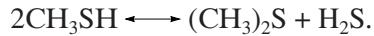


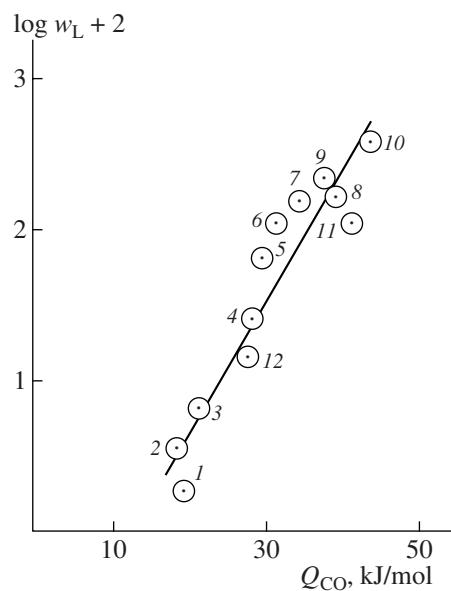
Table 3 compares the activities of the catalysts in dimethyl disulfide conversion and  $S_{\text{DMS}}$  data for  $T = 190^\circ\text{C}$  and  $X = 60\%$ . Under the action of weak L sites with  $Q_{\text{CO}} \leq 20 \text{ kJ/mol}$  and strong basic sites with  $PA^0 = 930\text{--}960 \text{ kJ/mol}$ , which are present in MgO, 2.3% Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>, and K<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>,  $S_{\text{DMS}}$  does not exceed 10%. On the catalysts containing L sites with  $Q_{\text{CO}} = 27\text{--}31 \text{ kJ/mol}$  along with strong basic sites, such as Al<sub>2</sub>O<sub>3</sub> modified with 0.04–0.23 wt % Na<sub>2</sub>O or 10%

K<sub>2</sub>WO<sub>4</sub>, the dimethyl sulfoxide formation rate and selectivity are higher. In the presence of the catalysts containing weak basic sites ( $PA^0 \leq 900 \text{ kJ/mol}$ ) and L sites of different strengths, the rate of dimethyl sulfide formation depends on the strength of the L sites. For instance, the reaction occurs at a low rate and is nonselective under the action of the weak L sites ( $Q_{\text{CO}} = 20\text{--}28 \text{ kJ/mol}$ ) present in NaX, Cr<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>. The parameters of the process improve with an increase in the strength of the L sites, for example, in the presence of some alumina catalysts. A linear dependence of the logarithm of  $w_L$  (dimethyl sulfide formation rate per total L site content) on the strength of the L sites is observed (Fig. 3). However, almost no formation of

**Table 3.** Conversion of dimethyl disulfide into dimethyl sulfide on acid catalysts at  $T = 190^\circ\text{C}$  and  $X = 60\%$

Catalyst	L sites, $Q_{\text{CO}}$ , kJ/mol ( $C$ , $\mu\text{mol}/\text{m}^2$ )	Protonic sites with $PA^0 < 1200 \text{ kJ/mol}$ ( $C$ , $\mu\text{mol}/\text{m}^2$ )	$w$ , mmol/(h (g Cat))	$S, \%$ ( $\text{CH}_3)_2\text{S}$ )
NaX	20 (3)	0	2.2	2
Cr <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	28 (0.4)	0.25	0.3	7
TiO <sub>2</sub>	42 (0.87)	0	1.0	6
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	32–36 (2.3); 41 (0.2)	~0.01	1.9	38
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> + H <sub>2</sub> S	34 (1.5)	~0.1	3.7	56
B <sub>2</sub> O <sub>3</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	27–35 (1.5); 40–51 (0.13)	0.07	1.8	48
$\eta$ -Al <sub>2</sub> O <sub>3</sub>	34 (1.6); 56 (0.1)	~0.02	3.0	52
H <sub>2</sub> SO <sub>4</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	37–48 (0.5)	0.09	0.3	11
H <sub>3</sub> PO <sub>4</sub> /SiO <sub>2</sub>	0	1.2*	0.5	0
HSiW/SiO <sub>2</sub>	0	1.0	0.16	23
HPW/SiO <sub>2</sub>	0	1.0	0.2	26
HPW/TiO <sub>2</sub>	0	2.5	0.8	28
HNaY	35 (0.06); 45–55 (0.1)	1.0	3.0	27
HZSM-5	32–38 (0.17); 42–53 (0.017)	0.33	6.1	54

\*  $PA^0 \sim 1300 \text{ kJ/mol}$ .



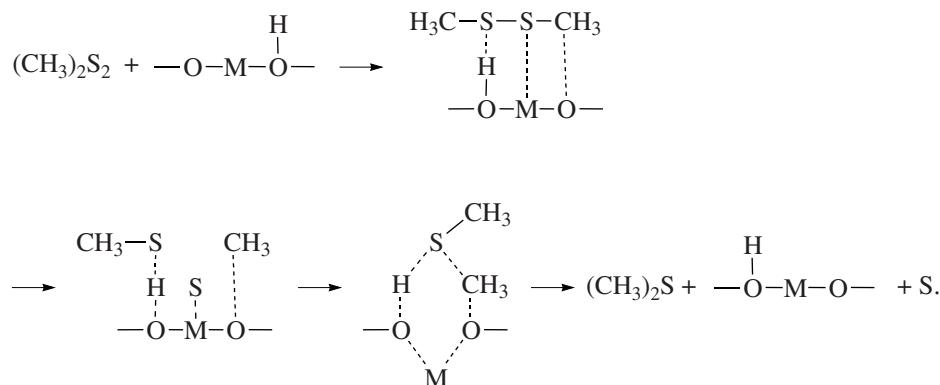
**Fig. 3.** Logarithm of  $w_L$  versus the strength of the L sites ( $Q_{CO}$ ) at  $190^\circ C$  for the catalysts (1)  $NaX$ , (2) 2.3%  $Na_2O/Al_2O_3$ , (3)  $MgO$ , (4) 0.23%  $Na_2O/Al_2O_3$ , (5) 0.04%  $Na_2O/Al_2O_3$ , (6)  $K_2WO_4/Al_2O_3$ , (7)  $\gamma + \chi-Al_2O_3$  (A-1), (8)  $\gamma-Al_2O_3$  (A-2), (9)  $B_2O_3/Al_2O_3$ , (10)  $\eta-Al_2O_3$ , (11)  $TiO_2$ , and (12)  $Cr_2O_3/SiO_2$ .

dimethyl sulfide occurs if the basic sites are completely deactivated in a catalyst containing strong L sites (for

instance, 10%  $H_2SO_4/Al_2O_3$ ) or if strong basic sites are present along with strong acid sites (as in  $TiO_2$ ). In the presence of  $SiO_2$  and  $H_3PO_4/SiO_2$ , which have only weak protonic sites, almost no dimethyl sulfide is formed. The rate of dimethyl sulfide formation on catalysts with strong protonic sites (phosphomolybdc or silicotungstic acids supported on  $SiO_2$  or  $TiO_2$ ) is one order of magnitude lower than that on catalysts containing strong L sites and basic sites of moderate strength. In the presence of  $\eta-Al_2O_3$  and  $B_2O_3/Al_2O_3$ , which contain both strong basic sites and strong L sites, the reaction occurs at a higher rate and selectivity than in the presence of  $\gamma-Al_2O_3$ . However, after  $\gamma-Al_2O_3$  is treated with an  $H_2S + H_2$  mixture at  $T = 400^\circ C$ , strong protonic sites appear on the surface, resulting in a twofold increase in the rate of disulfide conversion and a 1.5-fold increase in  $S_{DMS}$ . It is assumed that the surface needs the simultaneous presence of strong protonic and aprotic acid sites and basic sites of medium strength.

Even at a low temperature, the interaction of dimethyl disulfide with the catalyst leads to the cleavage of the weak S–S bond and the appearance of  $CH_3S$  groups on the surface. At elevated temperatures, these methanethio groups are converted into surface  $CH_3$ ,  $OH$ , and  $H_xCS$  groups, which are then involved in the formation of both dimethyl sulfide and by-products.

The formation of dimethyl sulfide from dimethyl disulfide is assumed to proceed according to the following scheme:



On the contact between dimethyl disulfide and the catalyst, the sulfur atom of one  $CH_3S$  group of the disulfide binds to a protonic site of the surface, the sulfur atom of the second  $CH_3S$  group binds to an L site, and the carbon atom of the  $CH_3$  group binds to a basic site. The decomposition of this surface complex results in the release of sulfur and in dimethyl sulfide formation. It is necessary for the surface to contain strong protonic sites capable of protonating the disulfide at the sulfur atom, strong L sites for the detachment of the second sulfur atom from the disulfide molecule, and basic sites for their coordination with  $CH_3$  groups. The latter

should be of moderate strength to favor the formation of surface methoxy fragments and, at the same time, not retard the subsequent  $O-CH_3$  bond cleavage in the complex that precedes dimethyl sulfide formation.

The highest activity and selectivity in dimethyl sulfide formation are shown by catalysts whose surface contains strong protonic and aprotic acid sites and basic sites of moderate strength. Activated  $\gamma-Al_2O_3$  and the high-silica zeolite HZSM-5 satisfy these requirements. In the presence of these catalysts,  $S_{DMS} \geq 65\%$  at the point of complete disulfide conversion.

**Table 4.** Conversion of dialkyl disulfides into thiophene in the presence of sulfide catalysts

Sulfide catalyst	T, °C	τ, s	Thiophene yield, mol %	Sulfide catalyst	T, °C	τ, s	Thiophene yield, mol %
Dibutyl disulfide				Diethyl disulfide			
V <sub>2</sub> O <sub>5</sub> S*	525	0.6	46	V <sub>2</sub> O <sub>5</sub> S*	560	0.6	17
MoO <sub>3</sub> S*	520	0	14	MoS <sub>2</sub>	580	10.0	17
MoS <sub>2</sub>	580	10	27	Fe <sub>2</sub> O <sub>3</sub> S*	450	6.0	27
Rh <sub>2</sub> S <sub>3</sub>	545	0.6	30	AlMo	500	3.0	12
Fe <sub>2</sub> O <sub>3</sub> S*	450	0.6	20	AlCoMo	590	1.0	17
	500	0.6	30	Cr <sub>2</sub> O <sub>3</sub> S/Al <sub>2</sub> O <sub>3</sub> *	560	3.0	31
	540	0.6	50	AlCrK	500	6.0	30
Cr <sub>2</sub> O <sub>3</sub> S*	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	Mixture of dimethyl and diethyl disulfides			
	550	4.4	62	AlCrK	550	6.0	9
	550	3.1	56	AlCrK	550	6.0	60
	550	1.5	45		550	12.0	13
	580	6	66		500	24.0	18
	600	6	70		600	24.0	19

\* Oxides sulfurized by hydrogen sulfide at  $T = 450^\circ\text{C}$ .

### SYNTHESIS OF THIOPHENE

The pyrolysis of diethyl and dibutyl disulfides without a catalyst at  $T = 450\text{--}650^\circ\text{C}$  yields thiophene. The reaction proceeds via a free radical mechanism to form large amounts of gaseous products and resin [17, 18]. The parameters of the process improve considerably in the presence of solid catalysts (Table 4).

Our experiments [18–20] have demonstrated that diethyl and dibutyl disulfides are converted into unsubstituted thiophene on different catalysts at  $P = 0.1 \text{ MPa}$  and  $T > 400^\circ\text{C}$ . The rate of thiophene formation from dibutyl disulfide is ~2 times higher than in the case of diethyl disulfide. The catalytic process of thiophene formation is complicated by disulfide cracking yielding  $\text{H}_2\text{S}$  and hydrocarbons. It follows from kinetic measurements that the thiophene formation rate increases in proportion to the increase in the disulfide concentration; i.e., the reaction is first-order. No changes are observed in the selectivity with respect to thiophene and cracking products as the disulfide conversion changes, indicating that these reactions are parallel.

The conversion of diethyl and dibutyl disulfides was studied in the presence of oxide and sulfide catalysts. At the initial stage of the reaction, the metal oxides mainly accelerate the decomposition of the starting disulfide with  $\text{H}_2\text{S}$  and hydrocarbon evolution and thiophene forms in a very low yield. At later stages of the process,

the oxide is sulfided under the action of the sulfur-containing reaction medium to increase the catalytic activity in thiophene formation up to the values observed in the presence of the sulfide catalyst. For example, at  $T = 580^\circ\text{C}$  and  $\tau = 3 \text{ s}$ , as dibutyl disulfide (DBDS) is passed through the AlCrK catalyst in oxide and sulfide forms, the thiophene yield ( $y, \text{ mol } \%$ ) is as follows:

DBDS passed, mmol/(ml Cat)	0.1	0.3	0.6	0.9	1.4	1.7
$y, \text{ mol } \%$ for the catalyst in oxide form	0	2	11	19	27	26
sulfide form	32	29	31	29	31	29

The presence of sulfur and its reactivity are both essential for the activity of the catalyst. The reciprocal temperature ( $1/T (\text{K})^{-10}$ ) at which the rate of  $\text{H}_2\text{S}$  evolution upon catalyst reduction with hydrogen is  $0.06 \text{ mmol h}^{-1} (\text{g Cat})^{-1}$  was taken to be a measure of stability of the bond between sulfur and the catalyst surface (“sulfur mobility,”  $q_S$ ). Studies of the catalyst composition by chemical, thermal, and X-ray diffraction analyses showed that chemisorbed sulfur is the most reactive [21]. As is clear from Fig. 4, the logarithm of the rate constant of thiophene formation depends linearly on the “sulfur mobility” on the catalyst surface.

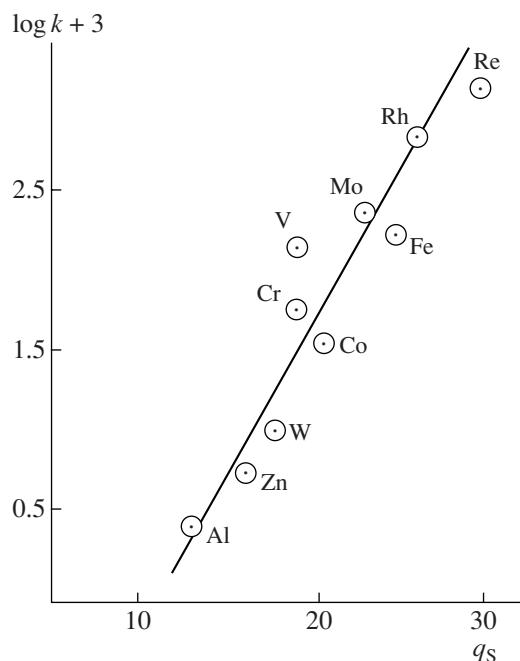
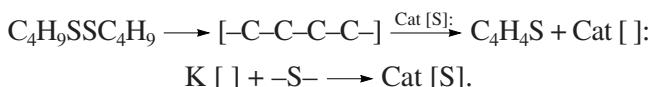


Fig. 4. Logarithm of the rate constant of thiophene formation versus the “sulfur mobility” on sulfide catalysts.

The following mechanism of thiophene formation is suggested. At a high temperature, the disulfide is chemisorbed dissociatively by the catalyst surface to cleave the S–S and C–S bonds and to form sulfur and hydrocarbon fragments, which can be involved in dehydrogenation, condensation, and other reactions. The resulting  $C_4$  hydrocarbon fragments interact with the surface sulfur atoms to form thiophene. The disulfide interacts with the catalyst depleted in sulfur and restores its steady-state content on the surface. The adsorption and desorption stages, cracking, condensation, the dehydrogenation of the hydrocarbon fragments, and the resulfurization of the catalyst occur at higher rates than the interaction of the dehydrogenated fragments with the sulfur atom on the catalyst surface:



In diethyl disulfide conversion, the initially formed hydrocarbon fragments are dimerized into  $C_4$  intermediates and then the reaction occurs in the same way as in the case of dibutyl disulfide.

The activity of the catalysts in disulfide cyclization into thiophene decreases during the reaction. The amount of thiophene formed on various catalysts before their complete deactivation is 0.05–0.1 mmol/( $m^2$  Cat.). Coke was observed on the deactivated catalyst surface, whose formation was likely, due to the deep cracking of disulfide destruction products. The amount of coke increases steadily with the reaction time. Coke deposition on the catalyst decreases the reaction rate and “sulfur mobility” on the surface. The results of dibutyl disulfide cyclization into thiophene at  $T = 520^\circ\text{C}$  on the  $\text{MoO}_3\text{S}$  catalyst are presented below:

$w/w_0$ , %	100	85	62	41	24	8
$q_s$	23	20	15	10	6	2

( $w$  and  $w_0$  are the thiophene formation rates at a given time and at the initial point in time, respectively). It was found that the initial activity of the deactivated catalysts can be restored by subjecting them to oxidative regeneration at  $T = 550^\circ\text{C}$ .

The sulfides of Re, Mo, Cr, Fe, and platinum group metals, both unsupported and supported on nonacidic alumina or an aluminosilicate, are the most active in thiophene formation. Aluminum–chromium–potassium (AlCrK) catalysts are particularly efficient: in their presence at  $T = 540$ – $560^\circ\text{C}$  and  $\tau = 3$ – $6$  s, the yield of thiophene from diethyl and dibutyl disulfides reaches 37 and 64 mol %, respectively.

Both individual disulfides and their mixtures can be used in thiophene synthesis (Table 4). Thiophene ( $y = 20$  mol %) and methylthiophene ( $y \approx 3$  mol %) were obtained on an AlCrK catalyst at  $T = 450$ – $600^\circ\text{C}$  and  $\tau = 24$  s from “disulfide oil” (mixture of dimethyl and diethyl disulfides) isolated from the gas desulfurization products. The decreased thiophene yield is probably due to the difficulties in the formation of  $C_4$  hydrocarbon fragments from dimethyl disulfide. Since thiophene formation from dialkyl disulfides proceeds through the formation of the hydrocarbon fragments, the thiophene yield from low-molecular-weight disulfides can be increased by adding a  $C_4$  to the reaction mixture. Thiophene is known to form when butane, butylene, or divinyl is passed through a sulfide catalyst [20, 22]. This reaction proceeds via the formation of  $C_4$  hydrocarbon fragments and their interaction with surface sulfur followed by the resulfurization of the catalyst by a sulfur-containing compound. Indeed, our experiments showed that thiophene forms in a higher yield of 60 mol % (Table 4) in the conversion of a mixture of “disulfide oil” with butylene (in a twofold molar excess) on the AlCrK catalyst.

#### SYNTHESIS OF THIOLSULFINATES, THIOLSULFONATES, AND SULFONIC ACIDS

Complexation between dialkyl disulfides and compounds containing acceptor sites involves one sulfur atom [23], which is activated and becomes capable of reacting with active oxygen. When the intensity of the donor–acceptor interaction is low, the process occurs without bond cleavage in the disulfide molecule and can afford mild-oxidation products, namely, thiolsulfonates and thiolsulfonates. Under certain conditions, complex formation at the sulfur atom also results in the cleavage of the weak S–S bond and in the formation of an RS structure, whose oxidation can yield a deeper oxidation product, namely, an alkanesulfonic acid. The

**Table 5.** Oxidation of diethyl disulfide in the gas phase at  $P = 0.1$  MPa

Catalyst	$T, ^\circ\text{C}$	$\tau, \text{s}$	$X, \%$	$S, \%^*$		Catalyst	$T, ^\circ\text{C}$	$\tau, \text{s}$	$X, \%$	$S, \%^*$			
				MO**	$\text{SO}_2$					MO**	$\text{SO}_2$		
$\text{O}_2/(\text{C}_2\text{H}_5)_2\text{S}_2 = 100 : 1$													
$\text{V}_2\text{O}_5$	180	5.7	10	60	38	$\text{V}_2\text{O}_5$	$\text{O}_2/(\text{C}_2\text{H}_5)_2\text{S}_2 = 5 : 1$	$\text{V}_2\text{O}_5$	220	6.7	19	36	63
	220	2.8	31	10	91				220	18	34	12	90
	220	5.2	75	1	96				220	2.3	25	80	0
	220	17.4	83	0	99				220	14.0	24	28	50
	260	2.4	50	1	98				220	2.6	6	27	0
$\text{K}/\text{V}_2\text{O}_5$	220	6.1	35	21	78	$\text{VOSO}_4$	220	$\text{HSiW}/\text{SiO}_2$	180	6.0	8	98	0
$\text{CuO}$	200	6.0	63	6	49	$\text{CuCl}_2/\text{SiO}_2$	220	$\text{VO}(\text{acac})_2\text{SiO}_2$	220	19.6	26	52	25
$\text{Cr}_2\text{O}_3$	200	6.2	40	13	86	$\text{CuSO}_4$	220		220	14.8	56	17	41

\*Minor amounts of ethanesulfonic acid were also observed ( $S = 0.5\text{--}10\%$ ).

\*\*MO is the total selectivity with respect to the mild-oxidation products  $\text{RSOSR} + \text{RSO}_2\text{SR}$ .

latter can also result from the oxidation of reactive mild-oxidation products. The complete oxidation of the initial disulfide and the products of its partial oxidation with sulfur dioxide evolution is also probable.

The catalytic oxidation of dialkyl disulfides by oxygen was studied under different conditions [24–27].

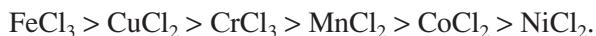
*Gas-phase oxidation of diethyl disulfide* was studied at  $P = 0.1$  MPa and  $T = 160\text{--}260^\circ\text{C}$  in the presence of solid acids and catalysts based on transition metal compounds. Selected results are presented in Table 5. In a large excess of oxygen over diethyl disulfide, the dominant reaction on V, Cr, and Cu oxides is complete oxidation with sulfur dioxide evolution. The partial-oxidation products, namely, ethanesulfonic acid, ethanethiol-sulfinate, and thiolsulfonate, form in smaller amounts. No sulfur and carbon balance is observed in many cases, and this is due to the accumulation of sulfonic acid on the catalyst surface [20]. A decrease in the oxygen content of the system exerts a favorable effect on the selectivity with respect to the mild-oxidation products (thiolsulfinate and thiolsulfonate). Along with the oxides, some transition metal compounds and supported acid catalysts are active in diethyl disulfide oxidation. On these catalysts, the reaction occurs in the same way as on the metal oxides, but, in some cases, the mild-oxidation product selectivity is higher.

On all of the solid catalysts, the disulfide conversion increases with an increase in the temperature, contact time, and oxygen-to-disulfide molar ratio. As follows from kinetic data, diethyl disulfide oxidation in the gas phase proceeds via a parallel-consecutive scheme: the disulfide is oxidized to thiolsulfinate, which is then converted into thiolsulfonate and sulfonic acid. Sulfonic acid can also form via the oxidation of RS structures resulting from disulfide dissociation, and  $\text{SO}_2$  is evolved as a result of the complete oxidation of the disulfide and, possibly, the oxidation of the partial-oxidation products. The best results for the gas-phase oxida-

tion of diethyl disulfide into mild-oxidation products ( $S = 36\text{--}98\%$  at  $X \leq 25\%$ ) are obtained at a low oxygen concentration on the  $\text{VOSO}_4$ ,  $\text{HSiW}/\text{SiO}_2$ , and  $\text{V}_2\text{O}_5$  catalysts. Drawbacks of the gas-phase process are the low selectivity with respect to the partial-oxidation products, the occurrence of complete oxidation, and catalyst deactivation by the reaction medium.

*Liquid-phase oxidation.* The oxidation of diethyl disulfide under air pressure ( $P = 5$  MPa) at  $T = 120\text{--}150^\circ\text{C}$  in various solvents (water, ethyl and isopropyl alcohols, acetone, and dioxane) was studied in the presence of the solid and dissolved catalysts. Selected results are listed in Table 6. When the reaction is carried out in acetone on  $\text{V}_2\text{O}_4$ ,  $\text{V}_2\text{O}_5$ , and  $\text{Cr}_2\text{O}_3$ , the ethanesulfonic acid yield is  $\sim 100$  mol %. An analysis of the liquid oxidation product by ESR and atomic absorption spectrophotometry showed the presence of vanadium or chromium ions in the solution. It is likely that the oxides partially dissolve by reacting with the sulfonic acid that has formed under the action of the solid catalyst and then the reaction occurs not only on the surface, but also in the solution. The oxidation of diethyl disulfide into sulfonic acid with  $S = 100\%$  also occurs on the hydrogen form of the cation exchanger at  $T = 140\text{--}150^\circ\text{C}$ . An induction period is observed, after which the rate of sulfonic acid formation increases sharply. The acceleration of the process is due to the extra effect of the resulting sulfonic acid. This was established by special-purpose experiments in which sulfonic acid was added to the reaction mixture.

Sulfonic acid was also the dominant product in the liquid-phase oxidation of diethyl disulfide in acetone in the presence of transition metal chlorides. The rate of sulfonic acid formation on these catalysts at an incomplete disulfide conversion decreases in the order



**Table 6.** Liquid-phase oxidation of dialkyl disulfides by atmospheric oxygen

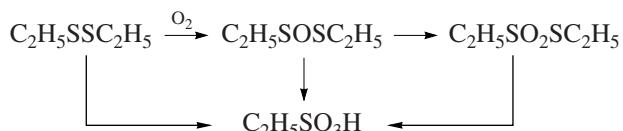
Catalyst	T, °C	t, min	X, %	S, %	
				MO*	RSO <sub>3</sub> H
Oxidation in acetone solution					
V <sub>2</sub> O <sub>5</sub>	140	120	96	0	100
V <sub>2</sub> O <sub>4</sub>	140	60	100	0	100
Cr <sub>2</sub> O <sub>3</sub>	140	60	95	0	100
Cation exchanger	140	60	100	0	100
Cation exchanger**	150	60	97	0	100
CuCl <sub>2</sub>	140	15	100	8	80
CuCl <sub>2</sub> *	140	15	84	2	98
CrCl <sub>3</sub>	140	60	100	0	100
FeCl <sub>2</sub>	140	20	100	0	100
VOCl <sub>2</sub>	140	20	100	1	98
VO(acac) <sub>2</sub>	120	60	92	1	97
	140	15	71	1	85
Oxidation in dichloroethane solution					
VO(acac) <sub>2</sub>	120	60	45	96	4
	140	60	52	93	6
VO(acac) <sub>2</sub> **	150	120	37	95	0

\*MO is the total selectivity with respect to the mild-oxidation products RSOSR + RSO<sub>2</sub>SR.

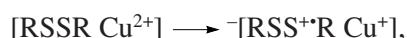
\*\*Disulfide concentrate oxidation; in the other cases, diethyl disulfide oxidation.

Vanadyl acetylacetone (VO(acac)<sub>2</sub>) in dichloroethane turned out to be particularly efficient in partial dialkyl disulfide oxidation: at  $T = 120\text{--}140^\circ\text{C}$ ,  $t = 30\text{--}60$  min, and  $X = 37\text{--}52\%$ , the disulfide oxidizes mildly into ethanethiolsulfinate and ethanethiolsulfonate with  $S =$

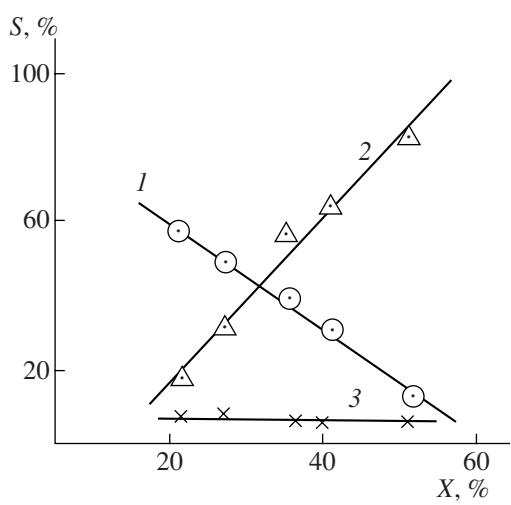
50–95%. Kinetic experiments showed that the thiolsulfinate selectivity decreases and the thiolsulfonate selectivity increases with an increase in the conversion. The disulfide conversion does not exert any significant effect on the sulfonic acid selectivity (Fig. 5). Partial oxidation on this catalyst likely proceeds according to the following scheme:



It is assumed that the partial oxidation of the disulfide in the liquid phase on the transition metal complexes proceeds via the mechanism proposed for the oxidation of dialkyl sulfides [22]. No bond cleavage occurs in the disulfide molecule during the formation of the complex with the catalyst, and only electron density redistribution takes place, yielding a positive charge on the sulfur atom, as is exemplified by oxidation in the presence of a divalent copper compound:



In an oxidative medium, the radical cation is converted into a peroxide, which reacts with the disulfide, turning into thiolsulfinate and then into thiolsulfonate via a sim-



**Fig. 5.** Selectivity with respect to (1) thiolsulfinate, (2) thiolsulfonate, and (3) sulfonic acid at different diethyl disulfide conversions. The catalyst is vanadyl acetylacetone, the solvent is dichloroethane,  $T = 140^\circ\text{C}$ , and  $P = 5$  MPa.

ilar mechanism. The copper ion reduced owing to complex formation is reoxidized by oxygen.

Experiments showed that the main products of liquid-phase diethyl disulfide oxidation in the presence of transition metal compounds are either thiolsulfinate and thiolsulfonate (mild-oxidation) or sulfonic acid (deeper oxidation), depending on the reaction conditions. The sulfinate and sulfonate are obtained with  $S = 60$  and 80%, respectively, on vanadyl acetylacetone in a dichloroethane solution at  $X \leq 50\%$ , and sulfonic acid forms in 100% yield at complete disulfide conversion in the presence of vanadium and chromium oxides and the cation exchanger.

A mixture of disulfides can also be subjected to partial oxidation (Table 6). The disulfide concentrate ( $R = C_1-C_3$ ) isolated from the products of gas demercaptanization is oxidized by vanadyl acetylacetone in dichloroethane to give mild-oxidation products with a total yield of 95 mol %, and a mixture of sulfonic acids forms results in ~100% yield from oxidation in acetone in the presence of copper chloride or the cation exchanger.

Thus, the results presented in this review demonstrate that the catalytic conversions of lower dialkyl disulfides can produce various sulfur compounds in a preparative yield with a high desired-product selectivity. A deeper study of the observed reactions and search for other reactions will make it possible to develop new processes for the synthesis of valuable thio compounds by catalytic processing of readily available disulfides.

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