

Catalytic Synthesis of Dialkyl Sulfides from Dialkyl Disulfides

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Received December 27, 2016

Abstract—Dialkyl disulfides R_2S_2 where $R = Me, Et, \text{ or } Pr$, both as individual compounds and as their mixtures, isolated from petroleum products can turn into alkanethiols and dialkyl sulfides under the action of catalysts having strong acid sites and medium-strength basic sites on their surface. In a helium atmosphere, the main conversion products are alkanethiols, while dialkyl sulfides form in low yield at a selectivity of no higher than 20%. A much higher dialkyl sulfide selectivity is attained in the reaction involving methanol. The most efficient catalyst for this reaction is alumina, with which the dialkyl sulfide selectivity is up to 99%.

Keywords: dialkyl disulfides, alkanethiols, dialkyl sulfides, catalysts

DOI: 10.1134/S0023158417040115

INTRODUCTION

Dialkyl sulfides R_2S_2 where $R = Me, Et, \text{ or } Pr$ (methyl, ethyl, or propyl) can find application as flotation agents, odorants, and starting compounds for various organic syntheses. On the preparative scale, dialkyl sulfides are synthesized by reacting an alkyl halide with an alkali metal sulfide or alkanethiol and by reacting an alcohol or olefin with hydrogen sulfide or alkanethiol [1]. Expensive and un readily available chemicals are often used for this purpose, and the synthetic methods themselves are technologically rather inconvenient. The existing set of chemicals usable in these syntheses is insufficient for the large-scale production of dialkyl sulfides. Dialkyl disulfides, which result in vast amounts from the oxidative desulfurization of mercaptan-containing petroleum products and gas condensates, might become a readily available and cheap raw material for dialkyl sulfide synthesis. This process yields a mixture of lower dialkyl disulfides, which is referred to as disulfide oil (DSO). To date, DSO has found only limited application, and its utilization causes certain environmental problems [2–4].

Catalytic reactions involving dimethyl disulfide (DMDS) have been investigated in greatest detail [5]. Under the action of solid acid catalysts in a helium atmosphere, the dimethyl sulfide selectivity at 100% DMDS conversion is 50–60%, but in the presence of methanol the selectivity is much higher. As dialkyl disulfides are heated to $>300^\circ\text{C}$ in the absence of a catalyst, they undergo thermolysis to yield alkanethiols, hydrogen sulfide, carbon disulfide, unsaturated hydrocarbons, thiophene, and polysulfides. The thermolysis rate increases with an increasing molecular weight of the disulfide [5]. Comparative reactivity data

for DMDS and its homologues are lacking in the literature.

Here, we report a study of the gas-phase reaction in which dialkyl sulfides form over a number of solid acid–base catalysts from individual dialkyl disulfides and their mixture resulting from the desulfurization of petroleum products.

EXPERIMENTAL

The individual chemicals that were used in the experiments were reagent-grade. DSO was a mixture of dialkyl disulfides that had been obtained by the oxidative demercaptanization of petroleum products at the Novoufimsk Oil Refinery. It consisted of 34 wt % DMDS, 50 wt % diethyl disulfide, and 16 wt % methyl ethyl disulfide.

The catalysts and supports were commercial $\gamma\text{-Al}_2\text{O}_3$ samples ($S_{\text{BET}} = 275$ and $200 \text{ m}^2/\text{g}$), a 50% $\gamma\text{-}$ + 50% $\chi\text{-Al}_2\text{O}_3$ mixture ($S_{\text{BET}} = 250 \text{ m}^2/\text{g}$), a 50% $\gamma\text{-}$ + 40% $\chi\text{-}$ + 10% $\eta\text{-Al}_2\text{O}_3$ mixture ($S_{\text{BET}} = 230 \text{ m}^2/\text{g}$), SiO_2 ($S_{\text{BET}} = 260 \text{ m}^2/\text{g}$), and high-silica zeolite in H-form (HZSM-5, $\text{SiO}_2 : \text{Al}_2\text{O}_3 = 34$, $S_{\text{BET}} = 500 \text{ m}^2/\text{g}$). Prior to performing experiments, these materials were calcined in flowing dry air for 5 h at $500\text{--}530^\circ\text{C}$. Supported catalysts were prepared by incipient-wetness impregnation of pre-calcined supports with aqueous solutions of sodium hydroxide and chromium trioxide. Next, the catalysts were dried in air at 110°C for 5 h and were then heat-treated for 5 h. The finished catalysts contained 1.7 wt % sodium and 1.6 wt % chromium.

The acid–base properties of the catalysts were studied earlier by IR spectroscopy of adsorbed probe

Table 1. Acid-base properties of catalysts

Catalyst	Site strength/(Concentration, $\mu\text{mol}/\text{m}^2$)		
	protonic sites	Lewis acid sites	basic sites
$\text{Na}/\text{Al}_2\text{O}_3$	1200/(0.1–0.2)	18–20/(2–3)	830–960/(3.8)
SiO_2	1390/(2.8)	0	<800/(2–3)
Cr/SiO_2	<1200/(0.25)	28(0.4)	800–900/(2.1)
HZSM-5	1170–1180/(0.33)	33–37/(0.16) 42–54/(0.013)	800–900/(1.1)
$\gamma\text{-Al}_2\text{O}_3$	1170–1270/(0.03)	32–34/(2.2) 41–56/(0.2)	800–900/(2.5)

molecules [6, 7]. The strength of protonic sites (PS's) was estimated in kJ/mol units as the pyridine affinity of the proton; the strength of Lewis acid sites (L-sites), as the heat of adsorption of CO; the strength of basic sites (BS's), as the basic site affinity of deuterium in CDCl_3 . The concentration of sites, C , was expressed in $\mu\text{mol}/\text{m}^2$ units.

Catalytic tests were carried out at atmospheric pressure in a flow reactor with a fixed catalyst bed. Each test was performed with a fresh portion of a catalyst with a grain size of 0.25–0.5 mm. The system was thermostated, and the reactants, entrained from saturators by helium flowing out of a cylinder, were fed into the reactor brought to the preset temperature. The duration of each test was ~2 h.

The reaction mixture was sampled at intervals, and the concentration of gaseous products in the samples was determined as the mean for 2 or 3 samples. The data discrepancy did not exceed 10%. The products were identified by the GC–MS method using an Agilent 7000 GC/MS Triple Quad system (Agilent, United States) fitted with a capillary column (30 m \times 0.25 mm) filled with the HP-5MS phase. Quantitative analyses were carried out on an LKhM-8MD chromatograph (Russia) with a thermal-conductivity detector (2 m \times 3 mm column packed with Porapak Q + Porapak R (1 : 1), helium as the carrier gas). The residence time was taken to be equal to the ratio of the catalyst volume (cm^3) to the gas flow rate (cm^3/s) at room temperature and atmospheric pressure.

In the experiments on DSO, the total disulfide conversion X (%) was calculated as the ratio of the amount of reacted DSO to the initial total disulfide content. The conversion of individual dialkyl disulfides was determined as the ratio of the amount of reacted disulfide to its initial content. The yield of a particular product of the reaction (y , mol %) was estimated as the ratio of the concentration of the product to the initial disulfide concentration, and the product formation selectivity was estimated as the ratio of the product yield to the total disulfide conversion. The reaction rate was expressed in terms of the number of

millimoles of disulfide converted per gram of catalyst per hour.

RESULTS AND DISCUSSION

The catalysts examined in this study vary in their nature and in the strength and concentration of acid and basic sites (Table 1). Two series of experiments were carried out on each catalyst, one in a helium atmosphere and the other in a dialkyl disulfides–methanol mixture. By varying the residence time, we found the τ value at which the disulfide conversion was 70%. At this τ value, we determined the yields of reaction products and the disulfide conversion rates. The initial dialkyl disulfide concentration in all experiments was 0.7–0.8 vol %.

Data concerning the conversions of individual dialkyl disulfides over all of the catalysts are presented in Tables 2–4. The rate of conversion of individual disulfides decreases in the $\text{MeSSPr} > \text{Et}_2\text{S}_2 > \text{Me}_2\text{S}_2$ order.

In the presence of the $\text{Na}/\text{Al}_2\text{O}_3$ catalyst, whose surface has no PS's but only weak L-sites and strong BS's, the major products at 200°C are alkanethiols: methanethiol forms from DMDS; ethanethiol, from diethyl disulfide; methanethiol and propanethiol, from methyl propyl disulfide. One of the DMDS conversion products is dimethyl sulfide, but its yield is low. The conversion of various disulfides is accompanied by the release of hydrocarbons, hydrogen sulfide, and carbon disulfide. Heating the reaction mixture to 350°C increases the conversion rate, but the dialkyl sulfide selectivity remains low.

The other catalysts contain medium-strength BS's and acid sites of various strengths at various concentrations. On the SiO_2 surface, which has weak PS's, the disulfide conversion rate at 200°C is low. At 350°C, DMDS turns mainly into methanethiol and the dialkyl sulfide selectivity remains low. In the presence of the Cr/SiO_2 catalyst, which has strong PS's and weak L-sites, the disulfide conversion rate is higher than over SiO_2 , but the major reaction products

Table 2. DMDS conversion data

Catalyst	$w, \text{mmol h}^{-1} \text{g}^{-1}$	Yield, mol %			Me_2S selectivity, %
		MeSH	Me_2S	H_2S	
200°C, helium atmosphere					
$\text{Na}/\text{Al}_2\text{O}_3$	0.7	53	12	5	17
SiO_2	0.1	2	0	1.5	0
Cr/SiO_2	0.2	26	1	2	3
HZSM-5	0.8	29	30?	10	44
$\gamma\text{-Al}_2\text{O}_3$	0.7	31	34	4	48
350°C, helium atmosphere					
$\text{Na}/\text{Al}_2\text{O}_3$	2.0	52	15	3	21
SiO_2	0.5	50	7	9	10
Cr/SiO_2	2.5	59	5	6	7
HZSM-5	3.5	40	16	14	23
$\gamma\text{-Al}_2\text{O}_3$	5.0	25	34	10	49
350°C, disulfide–methanol mixture*					
$\text{Na}/\text{Al}_2\text{O}_3$	2.1	61	3	4	7
SiO_2	0.5	50	7	11	10
Cr/SiO_2	1.7	60	6	3	9
HZSM-5	3.2	14	51	4	74
$\gamma\text{-Al}_2\text{O}_3$	2.2	0.7	69	0.3	98

* The methanol : disulfide molar ratio is $M = 2.5\text{--}3.2$.**Table 3.** Diethyl disulfide conversion data

Catalyst	$w, \text{mmol g}^{-1} \text{h}^{-1}$	Yield, mol %						Total sulfide selectivity, %
		MeSH	EtSH	Me_2S	MeSEt	Et_2S	H_2S	
200°C, helium atmosphere								
$\text{Na}/\text{Al}_2\text{O}_3$	0.9	0	55	0	0	0	14	0
SiO_2	0.1	0	0	0	0	0	3	0
Cr/SiO_2	0.4	0	45	0	0	0	24	0
HZSM-5	0.8	0	57	0	0	0	11	0
$\gamma\text{-Al}_2\text{O}_3$	1.7	0	48	0	0	0.5	20	0.7
350°C, helium atmosphere								
$\text{Na}/\text{Al}_2\text{O}_3$	2.6	0	62	0	0	0.5	6	0.7
SiO_2	0.9	0	50	0	0	0	19	0
Cr/SiO_2	3.5	0	53	0	0	7	8	10
HZSM-5	3.2	0	40	0	0	5	23	7
$\gamma\text{-Al}_2\text{O}_3$	4.4	0	48	0	0	9	12	17
350°C, disulfide–methanol mixture*								
$\text{Na}/\text{Al}_2\text{O}_3$	2.6	19	42	0	0	0	9	0
SiO_2	0.7	0	53	0	2	0	13	3
Cr/SiO_2	2.9	3	51	0	0	0	17	0
HZSM-5	4.3	3	7	40	11	6	2	81
$\gamma\text{-Al}_2\text{O}_3$	4.4	0	0	14	55	0	0	99

* The methanol : disulfide molar ratio is $M = 2.5\text{--}3.2$.

Table 4. Methyl propyl disulfide conversion data

Catalyst	w , mmol g ⁻¹ h ⁻¹	Yield, mol %						Total sulfide selectivity, %
		MeSH	PrSH	Me ₂ S	MeSPr	Pr ₂ S	H ₂ S	
200°C, helium atmosphere								
Na/Al ₂ O ₃	2.1	20	38	0	0	0	10	0
Cr/SiO ₂	0.6	0	42	0	20	0	6	0
HZSM-5	1.6	16	27	0	0	0	25	0
γ-Al ₂ O ₃ *	5.5	21	47	0	0	0	1	0
350°C, disulfide–methanol mixture**								
Na/Al ₂ O ₃	2.8	30	35	0	0	0	5	0
Cr/SiO ₂	1.7	59	0	3	0	0	7	4
HZSM-5	4.7	12	10	40	3	0	5	61
γ-Al ₂ O ₃	4.9	0	0	32	37	0	0	99

* The reaction was carried out at $T = 350^\circ\text{C}$.

** The methanol : disulfide molar ratio is $M = 2.5\text{--}3.2$.

Table 5. Disulfide oil conversion data

Catalyst	w , mmol g ⁻¹ h ⁻¹	Yield, mol %					Total sulfide selectivity, %
		MeSH	EtSH	Me ₂ S	MeSEt	H ₂ S	
350°C, helium atmosphere							
Na/Al ₂ O ₃	4.8	34	24	5	0	7	7
SiO ₂	0.6	46	11	1.5	0.7	9	7
Cr/SiO ₂	2.3	40	14	2	2	11	6
HZSM-5	1.6	46	13	6	1	2	10
γ-Al ₂ O ₃	2.6	43	9	10	3	3	19
350°C, DSM–methanol mixture*							
Na/Al ₂ O ₃	1.8	50	0	12	2	5	20
SiO ₂	0.8	42	10	11	2	3	18
Cr/SiO ₂	1.7	61	0	7	1	1	12
HZSM-5	2.6	30	0	25	10	4	50
γ-Al ₂ O ₃	1.9	0	0	44	25	0	99

* The methanol : disulfides molar ratio is $M = 2.5\text{--}3.2$.

are alkanethiols. The HZSM-5 catalyst contains considerable concentrations of strong PS's and strong L-sites. The conversion of various disulfides over this catalyst proceeds at an increased rate and the dialkyl sulfide selectivity is somewhat higher, but the alkanethiol yield is still significant. The γ-Al₂O₃ surface contains a high concentration of strong L-sites and a small quantity of strong PS's. In the presence of this catalyst, both alkanethiols and dialkyl sulfides form at a rather high rate. DMDS turns into dimethyl sulfide at a fairly high yield and nearly 50% selectivity. With the other catalysts, the sulfide selectivity is lower.

The conversion of the mixture of the disulfides present in DSO in a helium atmosphere over acid–

base catalysts proceeds in the same way as in the reactions involving individual disulfides. The sulfur-containing reaction products are methanethiol, ethanethiol, dimethyl sulfide, methyl ethyl sulfide, and hydrogen sulfide (Table 5). The conversion of each disulfide in the mixture is 1.5–2 times lower than the conversion of the same disulfide when it is alone. This is apparently due to the competitive chemisorption of the disulfides in their mixture. The sulfide yields for the HZSM-5 and γ-Al₂O₃ catalysts, which contain strong acid sites, are higher than for the other catalysts but do not exceed 20 mol %.

Experiments on DMDS conversion in a helium atmosphere over γ-Al₂O₃ at a fixed temperature

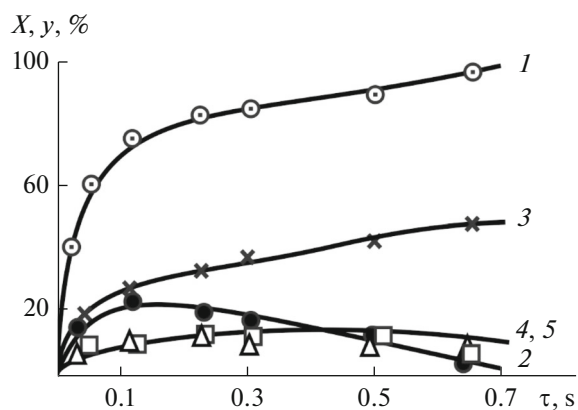


Fig. 1. Residence time effect on the (1) DMDS conversion, (2) methanethiol yield, (3) dimethyl sulfide yield, (4) hydrogen sulfide yield, and (5) carbon disulfide yield in the reaction of DMDS in a helium atmosphere over the γ - Al_2O_3 catalyst at 350°C .

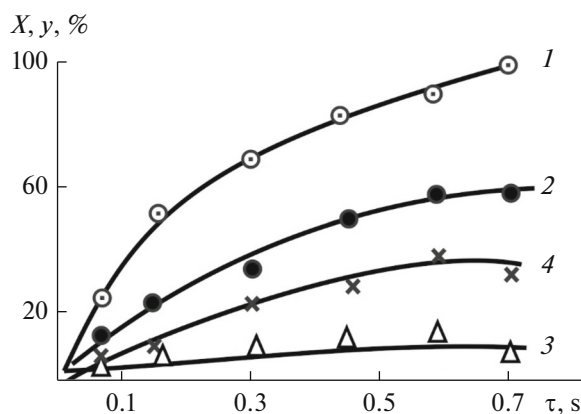


Fig. 2. Residence time effect on the (1) diethyl disulfide conversion, (2) ethanethiol yield, (3) diethyl sulfide yield, and (4) hydrogen sulfide yield in the reaction of diethyl disulfide in a helium atmosphere over the HZSM-5 catalyst at 350°C .

demonstrated that, with an increasing residence time, the DMDS conversion and dimethyl sulfide and by-product yields increase, while the methanethiol yield initially increases and then passes through a maximum and falls off (see, e.g., Fig. 1). It is likely that, as in the case of other acid-type catalysts [8], DMDS decomposes to yield methanethiol, which then disproportionates to dimethyl sulfide and hydrogen sulfide. Under our experimental conditions, the yield of dimethyl sulfide was close to its equilibrium yield [9]. In the reactions of DMDS homologues over catalysts having strong acid sites, an increase in τ causes an increase in the disulfide conversion and in the yield of all reaction products (see, e.g., Fig. 2 and Table 6). The product of diethyl disulfide decomposition is ethanethiol, and the decomposition of methyl ethyl disulfide and methyl propyl disulfide yields methanethiol, ethanethiol, and propanethiol. It is possible that the alkanethiols forming at the early stages of the reaction also disproportionate to H_2S and dialkyl sulfide, but the latter undergoes cracking. This process is known

[10] to proceed to a greater extent with an increasing molecular weight of dialkyl disulfide. The strength of the S–S bond is practically the same in various disulfides, but, owing to conjugation involving $3d$ orbitals of the dithio group, in the DMDS homologues proton abstraction from the methylene group adjacent to the S–S bond takes place more readily [5], leading to cracking. In addition, the initial dialkyl disulfides and the resulting alkanethiols and dialkyl sulfides decompose partially to release hydrogen sulfide and gaseous hydrocarbons.

It follows from the data of this study that, in the presence of acid–base catalysts, dialkyl disulfide conversion in a helium atmosphere cannot be made to afford dialkyl sulfides in high yield.

The interaction of dialkyl disulfides with methanol was investigated over the same catalysts as their conversion in helium. It was found earlier that the outcomes of the process (product yields and product selectivities) depend on the methanol-to-disulfide molar ratio (M). For example, the following results

Table 6. Conversion data for the DSO–methanol mixture in the presence of γ - Al_2O_3 at various residence times ($T = 350^\circ\text{C}$, $M = 2.5$ – 3.2)

τ , s	Dialkyl disulfide conversion, %				Yield, mol %		$\text{Me}_2\text{S} + \text{MeSEt}$ selectivity, %
	DSO	Me_2S_2	MeSSEt	Et_2S_2	Me_2S	MeSEt	
0.20	22	14	32	52	14	7	95
0.26	30	20	41	56	19	10	97
0.47	52	39	63	77	33	18	98
0.50	55	40	64	80	33	21	98
0.69	72	57	71	90	45	25	97
0.80	81	64	75	94	52	27	97
0.95	90	75	88	100	58	29	97

were obtained in the conversion of diethyl disulfide over $\gamma\text{-Al}_2\text{O}_3$ at 350°C and a residence time of $\tau = 0.5$ s:

Yield, mol %	<i>M</i>				
	0.5	1	2	3	4
$\Sigma\text{Me}_2\text{S} + \text{MeSEt}$	13	30	54	64	66
$\Sigma\text{MeSH} + \text{EtSH} + \text{H}_2\text{S}$	66	50	26	15	12

Clearly, as *M* is increased, the total dialkyl sulfide yield increases and the by-product yield decreases. At $M > 2$, the process is somewhat stabilized. The above data concerning the reactions in disulfide–methanol mixtures (Tables 2–6) were obtained at $M = 2.5\text{--}3.2$ and a temperature of 350°C .

The reactions of the disulfides with methanol occur over all of the catalysts examined. The products of the reactions are alkanethiols, dialkyl sulfides, hydrogen sulfide, carbon oxides, and dimethyl ether. Over $\text{Na}/\text{Al}_2\text{O}_3$, a catalyst with strong BS's and weak acid sites, the individual disulfides are converted at a fairly high rate. All methanethiol disulfides turn into alkanethiols, and the reactions of the disulfides containing an ethyl or propyl group yield ethanethiol and propanethiol as well. The dialkyl sulfide yield is extremely low. The catalyst containing only weak PS's and medium-strength BS's (SiO_2) shows a low activity in the reactions of the disulfides with methanol, and the products consist mainly of alkanethiols. The reaction over the catalyst having strong PS's, weak L-sites, and medium-strength BS's (Cr/SiO_2) occurs in a similar way, but its rate is higher than in the case of silica. The presence of strong acid sites on the catalyst surface (as in HZSM-5 and $\gamma\text{-Al}_2\text{O}_3$) markedly increases the reaction rate and favors the formation of dialkyl sulfides in high yield. The reaction over the zeolite is complicated by alkanethiol formation, and the reaction over $\gamma\text{-Al}_2\text{O}_3$ practically yields only sulfides. Dimethyl sulfide forms from all of the disulfides, and the reactions of diethyl disulfide and methyl propyl disulfide yield sulfides with $\text{R} = \text{Me}$, Et , and Pr as well (see, e.g., Fig. 3). The dimethyl sulfide yield decreases in the $\text{MeSSPr} > \text{Et}_2\text{S}_2 > \text{Me}_2\text{S}_2$ order. This is likely due to the fact that the DMDS homologues undergo cracking more readily to release hydrogen sulfide, which then reacts with methanol, yielding dimethyl sulfide. The reactions of methanol with the disulfides contained in DSO occur in the same way as the reactions of the individual disulfides, but the rate of conversion of the petroleum disulfides mixed with methanol is 1.5–2 lower than the rate of their conversion in a helium atmosphere. In the reactions catalyzed by $\text{Na}/\text{Al}_2\text{O}_3$, SiO_2 , or Cr/SiO_2 , the main products are alkanethiols and the dialkyl sulfide selectivity is low. However, the selectivity is much higher in the reactions catalyzed by zeolite HZSM-5 or $\gamma\text{-Al}_2\text{O}_3$.

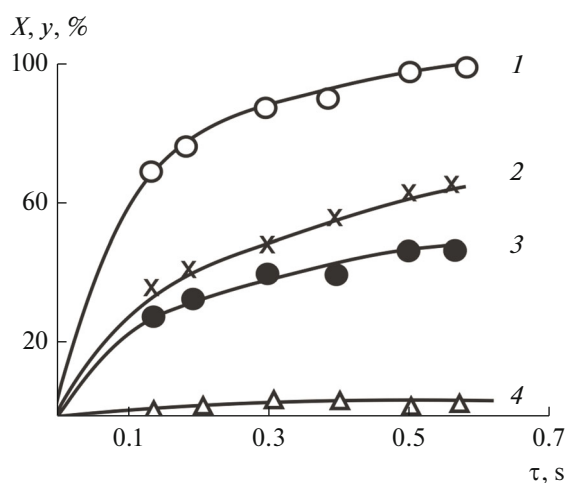


Fig. 3. Residence time effect on the (1) methyl propyl disulfide conversion, (2) methyl propyl sulfide yield, (3) dimethyl sulfide yield, and (4) hydrogen sulfide yield in the reaction of the methyl propyl disulfide–methanol mixture over the $\gamma\text{-Al}_2\text{O}_3$ catalyst at 350°C .

Therefore, for the formation of dialkyl sulfides from dialkyl disulfides and methanol, it is necessary that the catalyst surface contain high concentrations of strong L-sites and medium-strength BS's and some quantity of strong PS's. High concentrations of the latter enhance the formation of alkanethiols. The most efficient catalyst for the synthesis of dialkyl sulfides from methanol and dialkyl disulfides is alumina.

Methanol adsorption on the solid acid catalysts leads to the release of surface-bound CH_3 fragments [5, 11, 12]; disulfide adsorption, to the formation of RS fragments. The interaction of these fragments yields reaction products. Dimethyl, methyl ethyl, and methyl propyl sulfides result from the interaction of MeS , EtS , and PrS groups with the CH_3 fragment. In addition, part of the dialkyl disulfides and resulting thiols and sulfides decomposes to release hydrocarbons and hydrogen sulfide. The reaction between hydrogen sulfide and methanol produces methanethiol and dimethyl sulfide. The mechanism of the catalytic reaction producing dialkyl sulfides from dialkyl disulfides will be the subject of our further studies.

Using diethyl disulfide as an example, we investigated the interaction of the disulfides with methanol over alumina samples differing in their phase composition, porosity, specific surface area, and granule size. It was found that, for uncrushed catalyst granules, the observed rate of the reaction is independent of the gas hourly space velocity when the latter is not lower than 0.8 h^{-1} , but it increases markedly with an increasing temperature. Therefore, there are no external diffusion limitations in the process. The rate of the reaction over pure $\gamma\text{-Al}_2\text{O}_3$ is 1.4–3 times higher than over $\gamma\text{-Al}_2\text{O}_3$ containing χ - and $\eta\text{-Al}_2\text{O}_3$.

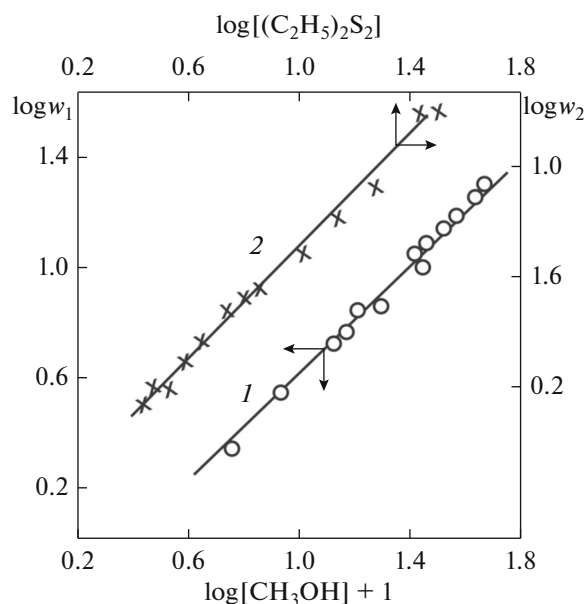


Fig. 4. Logarithmic plots of the (1) methanol and (2) diethyl disulfide conversion rates versus the concentration of the corresponding reactant for the reaction between diethyl disulfide and methanol over the $\gamma\text{-Al}_2\text{O}_3$ catalyst at 350°C .

For $\gamma\text{-Al}_2\text{O}_3$, the reaction rate is directly proportional to the specific surface area of the catalyst and increases as the size of transport pores increases from 70 to 100 nm and as the granule size is decreased from 4–5 to 0.25–0.5 mm. The surface of the $\gamma\text{-Al}_2\text{O}_3$ catalyst is practically fully used at a transport pore volume of $0.34\text{ cm}^3/\text{g}$, and at a smaller volume of these pores the catalyst use efficiency does not exceed 0.6–0.8.

We studied the effect of experimental conditions on the formation of dialkyl sulfides in the kinetically controlled reaction of methanol with disulfides over $\gamma\text{-Al}_2\text{O}_3$. The rate of the reaction was changed by varying the reactant concentrations. For example, in the reaction between diethyl disulfide and methanol at a fixed initial disulfide concentration, the methanol conversion rate increases in proportion to the current methanol concentration and the disulfide conversion rate at a constant initial CH_3OH concentration is directly proportional to the current disulfide concentration (Fig. 4). The reaction rate w is given by an equation that is first-order with respect to both methanol and diethyl disulfide:

$$w = kC_{\text{MeOH}}C_{\text{EtSSeEt}}$$

where k is the rate constant of the reaction.

As the residence time is extended, the conversion and the product yield at a fixed temperature increase.

The disulfide conversion has no effect on the dialkyl sulfide selectivity, indicating that the reaction routes are mutually independent. In the presence of $\gamma\text{-Al}_2\text{O}_3$, the dialkyl sulfide selectivity at 100% conversion reaches 99%.

CONCLUSIONS

Over the solid acid catalysts, at $T = 200\text{--}350^\circ\text{C}$ dialkyl disulfides, both individual and isolated from petroleum products, turn into alkanethiols and dialkyl sulfides. In a helium atmosphere, the dominant products are alkanethiols and the dialkyl sulfide selectivity is no higher than 20%. In the presence of methanol, the selectivity toward dialkyl sulfide formation under the action of the acid catalysts is substantially higher. With the alumina catalysts, which have strong Lewis acid sites, a small quantity of strong protonic sites, and medium-strength basic sites, the dialkyl sulfide selectivity at 100% dialkyl disulfide conversion is as high as 99%.

The results of this study can provide a basis for developing a new, selective process for the synthesis of dialkyl sulfides from individual disulfides or from their mixtures obtained by demercaptanization of petroleum products.

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