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Dimethyl Disulfide Conversion into Dimethyl Sulfide in the Presence of Sulfidized Catalysts

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Abstract—The conversion of dimethyl disulfide in the presence of various supported sulfidized metal-containing catalysts at atmospheric pressure and $T = 150$–$350°C$ was studied. Sulfidized transition metals supported onto aluminum oxide were more active than catalysts based on a carbon support, silicon dioxide, amorphous aluminosilicate, and zeolite ZSM-5. The most active catalyst was 10% Co/Al_2O_3 prepared with the use of cobalt acetate as an active component precursor and treated with a mixture of hydrogen sulfide with hydrogen at $T = 400°C$. From kinetic data, it follows that all of the reaction products were formed simultaneously at a temperature of <200°C, whereas a consecutive reaction scheme took place at higher temperatures. In the presence of a sulfidized alumina–cobalt catalyst, the output of dimethyl sulfide was higher than that reached with the use of other well-known catalysts.

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INTRODUCTION

Lower dialkyl disulfides are formed in considerable amounts upon the demercaptanization of fuels and gases [1]. In the presence of a number of catalysts, they can be converted into valuable substances, such as dialkyl sulfides and alkanethiols. In an atmosphere of hydrogen at $P = 0.1$ MPa and $T = 180$–$260°C$ in the presence of supported sulfidized catalysts containing Pd, Rh, Ru, Ni, Co, Mo, W, and Ni(Co)Mo, the hydrogenolysis of dimethyl disulfide (DMDS) and diethyl disulfide occurred at the S–S bond followed by the predominant formation of alkanethiols and dimethyl sulfide or diethyl sulfide in 0.2–10 mol % yields [2–7]. The yield of dialkyl sulfides considerably increased upon the conversion of dialkyl disulfides on oxide catalysts containing surface acid and basic sites in an inert atmosphere at $T = 190$–$350°C$. Previously [8], we found that catalysts on the surface of which medium-strength basic sites, strong protic acid sites, and strong aprotic acid sites occurred simultaneously were most active and selective in the conversion of DMDS into dimethyl sulfide. The sulfidization of the active component of an oxide catalyst and a change in its activity can occur in the course of reaction. The formation of dimethyl sulfide, which is a valuable thio compound, by the conversion of DMDS in an inert atmosphere in the presence of sulfidized catalysts was not studied previously.

In this work, we studied the regularities of the conversion of DMDS into dimethyl sulfide in the presence of sulfidized catalysts of various compositions in order to find an active and selective catalyst.

EXPERIMENTAL

The samples of γ-Al_2O_3 ($S_{BET} = 200$–275 m^2/g), γ-Al_2O_3 + χ-Al_2O_3 ($S_{BET} = 250$ m^2/g), η-Al_2O_3 ($S_{BET} = 300$ m^2/g), SiO_2 ($S_{BET} = 300$ m^2/g), amorphous AlSi ($S_{BET} = 360$ m^2/g), zeolite HZSM-5 (Si/AL = 17; $S_{BET} \sim 500$ m^2/g), and Sibunit activated carbon ($S_{BET} = 560$ m^2/g) were used as supports. The supported catalysts were prepared by the incipient wetness impregnation of precalcined supports with aqueous solutions of sodium hydroxide; potassium tungstate; tungstophosphoric acid; chromium nitrate; cobalt acetate, chloride, or nitrate; nickel chloride or nitrate; ammonium perrhenate; ruthenium hydroxychloride; palladium chloride; and ammonium heptamolybdate. Bimetallic catalysts based on nickel (cobalt) and molybdenum were prepared by the impregnation of aluminum oxide with aqueous solutions containing a mixture of nickel (cobalt) nitrate or chloride and ammonium heptamolybdate. All of the samples after impregnation were kept in air at room temperature for 12 h and dried at 110°C (5 h). The samples based on cobalt, nickel, ruthenium, and palladium chlorides were not calcined; the samples containing potassium tungstate and cobalt acetate were calcined at 400°C for 5 h, and the other samples were calcined at 500°C. In the text and the tables, element concentrations in weight percent are given before the symbols of the elements. Reagent-grade DMDS was used in the experiments.

The catalytic experiments were performed in a flow setup at atmospheric pressure. Helium from a gas cylinder was supplied to a thermostated saturator filled with DMDS. Then, the gas saturated with DMDS

Table 1. Comparison between oxide and sulfide catalysts in terms of activity and selectivity in the conversion of dimethyl disulfide ($T = 190$ and 250°C; $X = 60\%$)

Catalyst	Oxide catalyst			Sulfide catalyst		
	w, mmol h^{-1} × (g Cat)$^{-1}$	S, %	w_S, mmol h^{-1} × (g Cat)$^{-1}$	w, mmol h^{-1} × (g Cat)$^{-1}$	S, %	w_S, mmol h^{-1} × (g Cat)$^{-1}$
$T = 190°C$						
0.3 Na/Al_2O_3	1.1	20	0.22	2.0	48	1.0
γ-Al_2O_3	2.0	46	0.92	3.7	54	2
2.5 Cr/Al_2O_3	0.5	8	0.04	2.3	26	0.6
5 Mo/Al_2O_3	0.2	30	0.06	2.7	50	1.3
10 W/Al_2O_3	0.2	10	0.02	0.8	25	0.2
10 Co/Al_2O_3	0.4	14	0.16	3.2	26	1.2
5 Ni 10 Mo/Al_2O_3	0.3	10	0.03	2.4	28	0.56
$T = 250°C$						
Al_2O_3	8.2	40	3.3	16.3	54	8.8
2.5 Cr/Al_2O_3	4.2	16	0.7	18.9	30	5.2
5 Mo/Al_2O_3	1.7	15	0.26	17.4	44	7.6
10 W/Al_2O_3	6.4	26	1.7	13.8	40	5.5
10 Co/Al_2O_3	18.4	36	6.6	32	40	12.8
5 Co/C	0.4	3	0.01	1.2	6	0.1
5 Ni 10 Mo/Al_2O_3	1.6	10	0.16	10.3	35	3.6

arrived at a heated reactor with a catalyst. In the activity measurements, a fresh catalyst sample with a particle size of 0.25–0.5 mm was used in each particular experiment. The catalysts were either not activated additionally or treated with a mixture of 15% H_2S + 85% H_2 at $T = 400°C$ for 1 h (except for specified cases) and then purged with helium at the experiment temperature for 30 min before activity measurements. A mixture of DMDS with helium (the initial concentration of DMDS in the mixture was 1.6 ± 0.2 vol %) was passed through the reactor with the catalyst at a required temperature. Within 30 min after the onset of passing the mixture to the reactor, the initial mixture and reaction products were sampled for analysis; in the determination of catalyst stability, the samples were taken at regular intervals for 3 h.

The reaction products were identified by gas chromatography–mass spectrometry. The quantitative analysis was performed on an LKhM-8MD chromatograph with a katharometer (a column of 2 m × 3 mm packed with Porapak Q and Porapak R (1 : 1); helium was a carrier gas).

The ratio of the catalyst volume to the gas flow rate in cm^3/s at room temperature and atmospheric pressure was taken as the contact time (τ, s). Based on the results of analysis, the conversion of DMDS (X, %), the yields of reaction products (Y, mol %), the selectivity of dimethyl sulfide formation (S_{DMS}, %) as the Y/X ratio, and the rates of the overall reaction of DMDS at a specified DMDS conversion (w) and the formation of dimethyl sulfide (w_S) in mmol h^{-1} (g Cat)$^{-1}$ were calculated.

RESULTS AND DISCUSSION

The preliminary experiments were performed at $T = 190$ and 250°C in the presence of a number of oxide and sulfidized catalysts. Dimethyl sulfide, methanethiol, H_2S, CS_2, and C_1–C_2 hydrocarbons were the reaction products on all of the catalysts. Table 1 summarizes experimental results. At the same concentration of an active component, catalysts in the oxide form were much less active (by a factor of 2–14) in the formation of dimethyl sulfide than the sulfidized samples. The introduction of sodium hydroxide or transition metal (Mo, Cr, Co, and W) oxides into γ-Al_2O_3 resulted in a decrease in the rate of dimethyl sulfide formation, as compared with that observed on pure aluminum oxide. This may be due to a difference in the acid properties of catalyst surfaces [9, 10]. As we found previously [8], the presence of both medium-strength basic sites and strong acid sites on the surface is required for the formation of dimethyl sulfide from DMDS. The majority of the test catalysts contained medium-strength basic sites (PA° = 800–900 kJ/mol) and a small number of strong proton sites with $PA^k <$ 1300 kJ/mol. In pure γ-Al_2O_3, Al^{3+} cations are Lewis

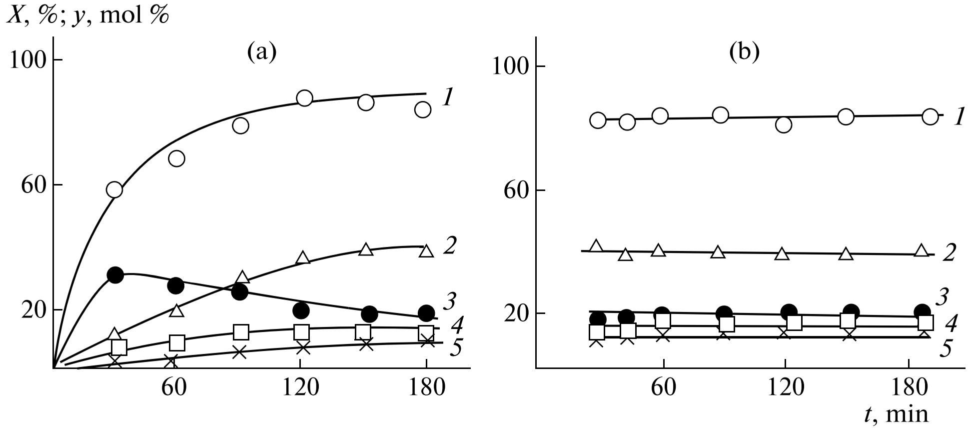

Fig. 1. Dependence of (*1*) DMDS conversion and the yields of (*2*) dimethyl sulfide, (*3*) methanethiol, (*4*) CS_2, and (*5*) H_2S on experiment time at $T = 250°C$. Catalyst: (a) oxide and (b) sulfidized forms of 10% Co/Al_2O_3.

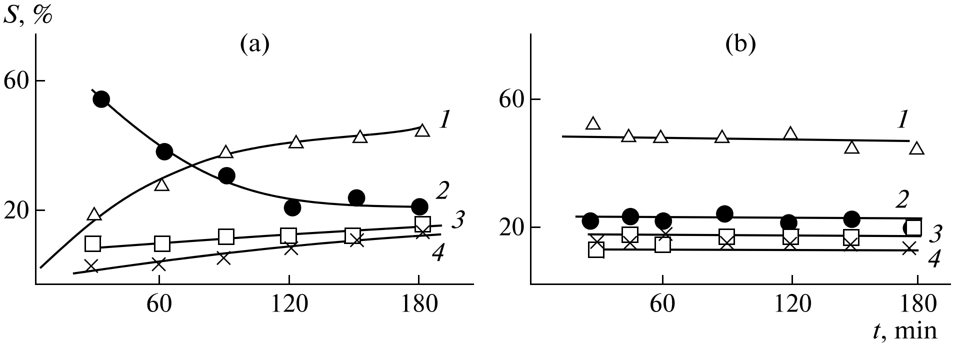

Fig. 2. Dependence of the selectivity of formation of (*1*) dimethyl sulfide, (*2*) methanethiol, (*3*) CS_2, and (*4*) H_2S on experiment time at $T = 250°C$. Catalyst: (a) oxide and (b) sulfidized forms of 10% Co/Al_2O_3.

acid sites (LASs). Upon the introduction of sodium hydroxide or transition metal oxides into γ-Al_2O_3, the LASs of alumina were blocked with the cations of Na, Mo, Co, Cr, and W oxides, which are weaker aprotic acids than Al^{3+} [9, 10]. This can result in a decrease in the rate of reaction and the selectivity of dimethyl sulfide formation. Upon the treatment of oxides with a mixture of $H_2S + H_2$ at an elevated temperature, the dissociative chemisorption of hydrogen sulfide occurred and the concentration of strong proton sites on the surface increased [9]. In addition, metal oxides under the action of H_2S can be partially converted unto sulfides and reduced at an elevated temperature with the formation of coordinatively unsaturated cations (strong acceptor sites), which participate in the activation of disulfide. Therefore, on sulfidized catalysts, the reaction of dimethyl sulfide formation occurred at an elevated rate, as compared with oxide catalysts.

In the course of reaction at $T = 190°C$ and a constant τ (contact time) on catalysts in oxide and sulfide forms, the values of X and the selectivity of product formation remained unchanged for 3 h. At 250°C, the conversion of DMDS and the yields of dimethyl sulfide and H_2S on oxide catalysts increased and the yield of methanethiol decreased as the experiment time was increased from 0.5 to 3 h. These characteristics remained unchanged as the reaction time was further increased. It is likely that oxides were sulfidized in the course of reaction under the action of the reaction atmosphere. This partially sulfidized oxide was much superior to the starting oxide catalyst in catalytic activity; however, even in a steady state, it was inferior to the sample treated with a mixture of $H_2S + H_2$ at $T = 400°C$, which was stable in operation (for example, see Figs. 1, 2).

The increase in the conversion of DMDS on various sulfidized catalysts at $T = 250°C$ resulted in an increase in the selectivity of dimethyl sulfide and H_2S formation and a decrease in the selectivity of methanethiol formation at the constant selectivity of CS_2 and C_1–C_2 hydrocarbon formation. The selectivity of hydrogen sulfide formation was lower than S_{DMS}; this was likely due to the participation of H_2S in the occurrence of side reactions (for example, see Table 2).

These results allow us to hypothesize that dimethyl sulfide is formed in accordance with a consecutive reaction scheme: DMDS interacts with surface protons and decomposes with the release of methanethiol, which then condenses with the formation of dimethyl sulfide and H_2S.

At DMDS conversions of <100%, the sulfidized catalysts differed in the selectivity of dimethyl sulfide formation; however, at $X \sim 100\%$, $S \approx 45–50\%$ on the majority of the catalysts.

Table 3 summarizes the results of the experiments performed on the sulfidized catalysts at $T = 250°C$ and various contact times. The catalysts based on Al_2O_3 exhibited higher activity and selectivity of dimethyl sulfide formation than the samples based on aluminosilicate, silica gel, or activated carbon. The γ-Al_2O_3 support treated with a mixture of $H_2S + H_2$ at $T = 400°C$ was active in the formation of dimethyl sulfide: at $X = 70\%$ $w = 12.2$ mmol h^{-1} (g Cat), $S = 50\%$, and $w_S = 6.1$ mmol h^{-1} (g Cat)$^{-1}$. The activity of the 2.3% Na/Al_2O_3 sample decreased by a factor of ~16, as compared with that of the parent support. After the introduction of Ru, Re, Ni, and Pd, the value of w decreased by a factor of 2.5–5. The activity of the samples containing Cr, Mo, and W differed only slightly from the activity of γ-Al_2O_3. Changes in the concentrations of Mo, Re, and Ru did not result in a noticeable increase in the rate of dimethyl sulfide formation. It is important that sulfidized alumina–cobalt catalysts were the most active species. The formation of dimethyl sulfide also occurred under the action of sulfidized bimetallic $Ni(Co)Mo/Al_2O_3$ catalysts; in this case, $NiMo/Al_2O_3$ was more active than $CoMo/Al_2O_3$ by a factor of almost 2; however, both of the catalysts were inferior to the monometallic sulfidized Co/Al_2O_3 and Mo/Al_2O_3 samples.

The S–S bond in dialkyl disulfides, in particular, in DMDS, is easily ruptured under the action of catalysts with the formation of CH_3S fragments. The methanethio fragments decompose to sulfur and surface CH_3 groups, the interaction of which can result in dimethyl sulfide [11]. In this case, the activity of sulfidized catalysts can depend on the binding energy of sulfur on the catalyst surface (the mobility of sulfur). We compared the mobility of surface sulfur, which was determined from the temperature of the onset of H_2S release on catalyst treatment with hydrogen (q_S, $1/T$, 10^4 K) [9], with the found rates of dimethyl sulfide formation in the presence of a number of sulfidized catalysts containing 5 wt % metal on aluminum oxide:

	A_2O_3	Co	Cr	Mo	W	Pd	Ni	Re
w_S, mmol/h (g Cat)	6.1	9.7	4.7	7.0	2.8	2.0	1.7	1.0
q_S, $1/T$, (K)	12.9	22.1	18.9	19.1	19.1	27.9	19.5	34.1

Sulfur is most strongly bound to the surface of alumina; the value of q_S for a cobalt catalyst is smaller by

Table 2. Selectivity of reaction product formation at various dimethyl disulfide conversions in the presence of the sulfidized 5 Cr/Al_2O_3 catalyst at $T = 250°C$

X, %	S, %			
	dimethyl sulfide	methanethiol	H_2S	CS_2
40	27	49	10	12
61	33	38	14	14
83	44	26	15	13
95	47	20	18	14
100	51	15	20	13

Table 3. Activity and selectivity of sulfidized catalysts in the conversion of dimethyl disulfide into dimethyl sulfide ($T = 250°C$; $X = 70\%$)

Catalyst	w, mmol × h^{-1} (g Cat)$^{-1}$	S, %	w_S, mmol × h^{-1} (g Cat)$^{-1}$
γ-Al_2O_3	12.2	50	6.1
2.3 Na/Al_2O_3	0.7	25	0.18
10 K_2WO_4/Al_2O_3	2.0	30	0.6
2.5 Cr/Al_2O_3	12.4	38	4.7
2.5 Cr/SiO_2	0.8	12	0.1
5 Mo/Al_2O_3	15.2	46	7.0
10 Mo/Al_2O_3	12.9	42	5.4
20 Mo/Al_2O_3	10.8	40	4.3
10 Mo/C	1.4	32	4.5
10 Mo/SiO_2	2.1	15	0.3
5 W/ Al_2O_3	6.1	46	2.8
10 W/Al_2O_3	12.9	44	5.7
18 W/Al_2O_3	6.2	35	2.2
10 W/C	0.7	14	0.1
5 Re/Al_2O_3	2.4	32	1.0
20 Re/Al_2O_3	3.4	32	1.1
5 Co/Al_2O_3	21.0	46	9.7
10 Co/Al_2O_3	30.0	46	13.8
10 Ni/Al_2O_3	4.7	35	1.7
5 Ru/Al_2O_3	3.3	35	1.2
10 Ru/Al_2O_3	1.2	20	0.24
5 Pd/Al_2O_3	7.5	27	2.0
2.5 Ni 10 Mo/Al_2O_3	12.5	35	4.2
2.5 Co 10 Mo/Al_2O_3	6.7	30	2.0

Table 4. Effect of the nature of an active component precursor on the activity and selectivity of sulfidized cobalt catalysts in the conversion of dimethyl disulfide into dimethyl sulfide ($T = 250°C$; $X = 70\%$)

Catalyst	Precursor	w, mmol h^{-1} (g Cat)$^{-1}$	S, %	w_S, mmol h^{-1} (g Cat)$^{-1}$
5 Co/AlSi	$CoCl_2$	3.5	26	0.9
	$Co(C_2H_3O_2)_2$	6.4	27	1.7
10 Co/Al_2O_3	$CoCl_2$	5.2	43	2.2
	$Co(NO_3)_2$	21.6	42	9.1
	$Co(C_2H_3O_2)_2$	30.0	46	13.8

Table 5. Effect of the nature of a support on the activity and selectivity of sulfidized cobalt catalysts in the conversion of dimethyl disulfide into dimethyl sulfide ($T = 250°C$, $X = 70\%$)

Catalyst	w, mmol h^{-1} × (g Cat)$^{-1}$	S, %	w_S, mmol h^{-1} × (g Cat)$^{-1}$	Support	w, mmol h^{-1} × (g Cat)$^{-1}$	S, %	w_S, mmol h^{-1} × (g Cat)$^{-1}$
10% Co/C	2.4	10	0.24	C	0.3	10	0.03
10% Co/SiO_2	4.5	6	0.3	SiO_2	0.15	7	0.01
10% Co/AlSi	6.5	22	1.4	AlSi	3.7	32	1.2
10% Co/HZSM-5	8.0	41	3.3	HZSM-5	14.1	40	5.6
10% Co/γ-Al_2O_3	30	46	13.8	γ-Al_2O_3	12.2	47	5.7
10% Co/η-Al_2O_3	21.8	45	9.8	η-Al_2O_3	7.2	48	3.4
10% Co/$(\gamma + \chi)$-Al_2O_3	10.2	48	4.9	$(\gamma + \chi)$-Al_2O_3	6.4	44	2.8

a factor of 1.7, and it is more active than Al_2O_3 in the formation of dimethyl sulfide by a factor of 1.6. The mobility of sulfur on the surface of samples containing Cr, W, Ni, and Pd is higher than that on aluminum oxide by a factor of 1.5–2; however, they are inferior to Al_2O_3 in the value of w_S by a factor of 1.3–3.6. The mobility of sulfur in the sulfidized Mo/Al_2O_3 catalyst is higher than that in Al_2O_3 treated with a mixture of $H_2S + H_2$; however, these catalysts differ only slightly in terms of activity. Sulfur is least strongly bound to the surface of rhenium sulfide; however, the 5% Re/Al_2O_3 catalyst is less active than Al_2O_3 by a factor of 6.1. Thus, the observed difference in the activities of sulfidized catalysts cannot be explained by different mobility of sulfur on their surfaces. It is likely that the reaction scheme of DMDS conversion into dimethyl sulfide on sulfidized catalysts is analogous to the scheme proposed previously for oxide catalysts [8]. Upon the chemisorption of DMDS on a catalyst, the sulfur atom of a CH_3S group is bound to a surface proton, the sulfur atom of the second CH_3S group is bound to an acceptor site (a coordinatively unsaturated metal sulfide cation), and the carbon atom of the CH_3 group is bound to a basic site. The decomposition of the surface complex leads to the release of sulfur and the formation of dimethyl sulfide. The increased concentration of coordinatively unsaturated cations on the surface of sulfidized catalysts is responsible for their higher activity in the formation of dimethyl sulfide, as compared with that of the oxide samples.

Among the test catalysts, the sulfidized cobalt catalysts exhibited the highest activity in the formation of dimethyl sulfide. The nature and concentration of a cobalt precursor, the type of the support, and the conditions of treatment with a mixture of $H_2S + H_2$ can affect their catalytic properties.

To reveal the effect of the nature of a catalyst precursor on process characteristics at $T = 250°C$, we determined the activity of cobalt samples prepared by the impregnation of supports with the solutions of cobalt chloride, nitrate, or acetate followed by sulfidization at $T = 400°C$ (Table 4). The 5% Co/AlSi catalyst, which was prepared with the use of cobalt chloride, was inferior to the catalyst prepared from cobalt acetate by a factor of 1.9 in terms of w_S. The 10% Co/AlSi catalyst (cobalt chloride as an active component precursor) was less active than that prepared with the use of cobalt nitrate by a factor of 4.1; however, the latter was inferior to the catalyst prepared from cobalt acetate by a factor of 1.5. The higher activity of the sulfidized alumina–cobalt catalysts prepared from cobalt acetate was due to a small size of cobalt-containing precursor particles on the support surface (1.5–2 nm). After the activation of supports impregnated with a solution of cobalt acetate, finely dispersed cobalt sulfide particles can be formed on the surface.

The effect of the nature of a support on the activity of cobalt catalysts sulfidized at 400°C was determined in experiments on the conversion of DMDS into dimethyl sulfide in the presence of catalysts prepared from cobalt acetate and containing 10 wt % Co on various supports: aluminum oxide, aluminosilicate, silica gel, activated carbon, and zeolite ZSM-5. As follows from data given in Table 5, the values of w_S on Co/C and Co/SiO_2 samples were lower than those in the presence of catalysts based on amorphous AlSi and zeolite HZSM-5 by a factor of 5–10. However, the latter catalysts were less active than the $Co/\gamma\text{-}Al_2O_3$ catalyst by a factor of 4–10. With the use of $\eta\text{-}Al_2O_3$ or $\gamma\text{-}Al_2O_3 + \chi\text{-}Al_2O_3$ as supports, which are structurally different from $\gamma\text{-}Al_2O_3$ [6], less active cobalt catalysts were prepared. To determine the contribution of a support to the activity of sulfidized cobalt catalysts, we performed experiments on aluminum oxide, silica gel, activated carbon, aluminosilicate, and zeolite ZSM-5, which were pretreated with a mixture of $H_2S + H_2$ at $T =$ 400°C. The carbon support and silica gel did almost not accelerate the reaction of DMDS conversion into dimethyl sulfide, whereas the sulfidized catalysts containing cobalt on these supports exhibited a noticeable activity. This fact allowed us to hypothesize that the reaction on these catalysts occurs under the action of cobalt sulfide rather than the support. Amorphous AlSi and zeolite HZSM-5 were equal in terms of activity or even somewhat superior to catalysts containing cobalt on these supports. It is likely that, on these catalysts, the reaction occurs on the support. In the presence of pure alumina, the reaction of dimethyl sulfide formation occurred at a sufficiently high rate (Fig. 3). At a Co concentration of ≤0.5 wt % on Al_2O_3, the activity of the sulfide catalyst was only slightly higher than that observed on the support. On $\gamma\text{-}Al_2O_3$ containing from 0.5 to 10 wt % Co, the values of w were higher than that on the pure support by a factor of 2–3. This fact suggests the occurrence of the formation of dimethyl sulfide mainly under the action of cobalt sulfide at an insignificant contribution from the support. At a cobalt sulfide content of >10 wt %, the activity of the catalyst decreased; this was likely due to a change in the dispersity of the active component.

The sulfidization temperature affected the activity of alumina–cobalt catalysts (Table 6). The rate of dimethyl sulfide formation on the 10% Co/Al_2O_3 catalyst prepared with the use of cobalt acetate without the treatment with a mixture of $H_2S + H_2$ was low; the value of w_S increased by a factor of ~3.5 or 7 after sulfidization at $T =$ 190–250 or 400°C, respectively. A further increase in the temperature to 450°C resulted in a dramatic decrease in the activity of the catalyst.

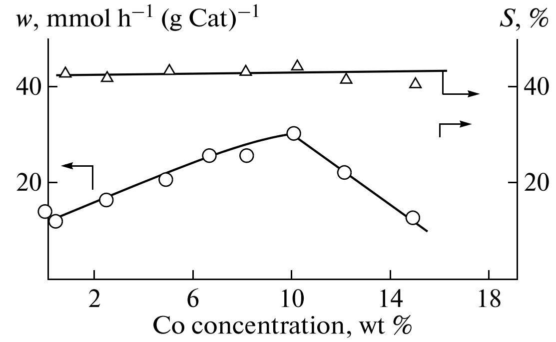

Fig. 3. Dependence of (*1*) the rate of DMDS conversion and (*2*) the selectivity of dimethyl sulfide formation at $X =$ 70% on sulfidized alumina–cobalt catalysts upon the cobalt content of the catalyst at $T =$ 250°C.

Thus, the sulfidized 10% $Co/\gamma\text{-}Al_2O_3$ catalyst prepared with the use of cobalt acetate as an active component precursor and treated with a mixture of $H_2S + H_2$ at $T =$ 400°C exhibited the highest activity in the formation of dimethyl sulfide from DMDS at $T =$ 250°C. The variation of reaction conditions on this catalyst demonstrated that, as the experiment temperature was increased, the rate of formation of dimethyl sulfide at X = 70% increased, whereas selectivity, which depends on contact time, decreased:

T, °C	150	170	200	220	250	300	330	350
w_S, mmol h^{-1} (g Cat)$^{-1}$	0.6	1.3	2.8	5.9	13.8	24.8	46.2	53.1
S, %	58	54	48	47	46	40	35	30

The kinetic experiments showed that the selectivity of product formation remained unchanged as the conversion of DMDS was increased at a constant initial concentration of DMDS and $T \le$ 200°C. It is likely that the products are formed from DMDS in independent reaction paths; that is, the reactions occur in parallel directions. At a higher temperature, the selectivity of dimethyl sulfide formation increased with DMDS conversion, whereas the selectivity of methanethiol formation decreased (Fig. 4). It is likely that, as on the other sulfidized samples, a consecutive reaction scheme occurs on the 10% $Co/\gamma\text{-}Al_2O_3$ catalyst at an elevated temperature: the decomposition of DMDS to methanethiol, which subsequently condensed to form dimethyl sulfide and hydrogen sulfide.

Table 6. Effect of the temperature of treatment of the 10% Co/Al_2O_3 catalyst with a mixture of $H_2S + H_2$ on its activity and selectivity the conversion of dimethyl disulfide into dimethyl sulfide ($T =$ 250°C; $X =$ 70%)

T, °C catalyst treatment with $H_2S + H_2$	w, mmol h^{-1} × (g Cat)$^{-1}$	S, %	w_S, mmol h^{-1} × (g Cat)$^{-1}$
–	5.0	38	1.9
190	16.6	38	6.3
250	18.7	39	7.3
400	30.0	46	13.8
450	11.6	44	5.1

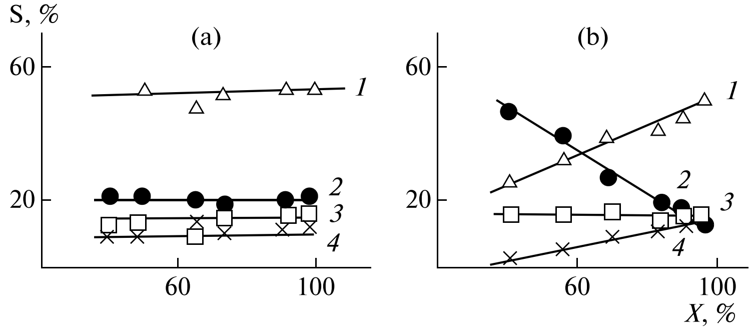

Fig. 4. Dependence of the selectivity of formation of (*1*) dimethyl sulfide, (*2*) methanethiol, (*3*) CS_2, and (*4*) H_2S on DMDS conversion. T = (a) 170 or (b) 250°C.

Based on the experimental data, we can conclude that sulfidized metal oxide catalysts and γ-Al_2O_3 are active in the reaction of dimethyl sulfide formation from DMDS. The 10% Co/γ-Al_2O_3 catalyst prepared with the use of cobalt acetate and treated with a mixture of $H_2S + H_2$ at $T = 400$°C was especially efficient. The formation of dimethyl sulfide in the presence of this sulfide catalyst occurred at a higher output, as compared with published data [8]; this allowed us to conclude that this catalyst is promising for the development of a new process for the synthesis of dimethyl sulfide.

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