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Hydrogenolysis of Dimethyl Disulfide to Methanethiol in the Presence of Cobalt Sulfide Catalysts

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Abstract—The hydrogenolysis of dimethyl disulfide to methanethiol at $T = 180–260°C$ and atmospheric pressure in the presence of supported cobalt sulfide catalysts has been studied. Cobalt sulfide on aluminum oxide exhibits a higher activity than that on a carbon support or silicon dioxide. The maximum reaction rate per gram of a catalyst is observed on an 8% Co/Al_2O_3 catalyst. At temperatures of up to 200°C and conversions up to 90%, methanethiol is formed with nearly 100% selectivity regardless of the cobalt content, whereas the selectivity for methanethiol under more severe conditions decreases because of its condensation to dimethyl sulfide.

INTRODUCTION

It is well known that the catalytic hydrogenolysis of disulfides with the rupture of S–S bonds and the formation of thiols can occur under the action of hydrogen. Transition metal sulfides, in particular, rhodium sulfide catalysts, are active in this reaction [1, 2]. It is reasonable to search for catalysts containing a less expensive and more active component. Thus, for example, it is well known that the reaction of disulfide hydrogenolysis occurs on cobalt sulfide. The reaction has been performed on bulk CoS catalysts at an elevated pressure of hydrogen: thiophenol was formed in 4% yield under the action of cobalt polysulfide ($T = 250–275°C$, $P = 21$ MPa) for 4 h at 100% diphenyl disulfide conversion [3]; under less severe conditions ($T = 90°C$, $P = 6$ MPa), 2,2'-dinitrodiphenyl disulfide was reduced to 2-aminothiophenol in 70% yield [4]. In the presence of bulk cobalt sulfide at $T = 150–155°C$ and $P = 6.3–14$ MPa in an atmosphere of hydrogen, dicyclohexyl sulfide and dibenzyl disulfide were converted into corresponding thiols in 55–93% yields [5]. The hydrogenolysis of disulfides to thiols can also occur on supported cobalt sulfide catalysts at a much lower pressure of hydrogen. Thus, in the presence of a 2.4% Co/Al_2O_3 sulfide catalyst at $T = 160°C$, $P = 0.3$ MPa, an H_2/disulfide molar ratio of 1 : 1, and a reaction time of 2 h, thiophenol was obtained with 100% selectivity; however, its yield was no higher than 5%, whereas the yield of thiophenol increased to 15% on a 2.4% Co–9.3% Mo/Al_2O_3 sulfide catalyst [6]. In the hydrogenolysis of diethyl disulfide on a 5% Co/Al_2O_3 sulfide catalyst at $T = 250°C$, $P = 0.1$ MPa, and a contact time (τ) of 0.08 s, ethanethiol was formed in 54% yield at 60% selectivity [1]. Previously [7, 8], the hydrogenolysis of dimethyl disulfide was studied at $T = 200°C$, $P = 0.1$ MPa, and an H_2/dimethyl disulfide ratio of 2 : 1 in the presence of various sulfide catalysts, including cobalt catalysts. On the 2.4% Co/Al_2O_3 and 2.4% Co–9.3% Mo/Al_2O_3 catalysts, which were prepared by the sulfurization of oxide samples, at $\tau = 0.05–0.08$ s, the yield of methanethiol was 5.5–11.8 mol % at 13–31% selectivity; dimethyl sulfide was also formed in 26–35% yield.

In this work, we studied the conversion of dimethyl disulfide into methanethiol in the presence of supported catalysts with various cobalt sulfide concentrations in order to find an active and selective cobalt catalyst for the synthesis of alkanethiols from dialkyl disulfides.

EXPERIMENTAL

The catalysts were prepared by the incipient wetness impregnation of precalcined supports (aluminum oxide ($S_{sp} = 240$ m^2/g), silicon dioxide ($S_{sp} = 300$ m^2/g), and a Sibunit C carbon support ($S_{sp} = 560$ m^2/g)) with an aqueous solution of cobalt chloride followed by drying in air and treatment with a mixture of 15% H_2S + 85% H_2 at $T = 250$ or 400°C for 1 h and then with hydrogen at an experiment temperature for 0.5 h. Reagent-grade or chemically pure chemicals were used in this study.

The catalytic experiments were performed at atmospheric pressure in a flow setup coupled to a chromatograph. Hydrogen from a gas cylinder was passed through a thermostated bubbler filled with dimethyl disulfide and then supplied to a heated reactor with a catalyst. The starting mixture and reaction products were sampled at regular intervals 0.5 h after the beginning of the experiment for analysis on an LKhM-8MD chromatograph with a thermal-conductivity detector (a column (2 m × 3 mm) packed with Porapak Q and Porapak R (1 : 1); helium was the carrier gas). A fresh catalyst sample with a particle size of 0.25–0.5 mm was used in each particular experiment. The ratio of the catalyst volume (cm^3) to the gas flow rate (cm^3/s) at room temperature and atmospheric pressure was taken to be the contact time. The value of τ was changed by varying

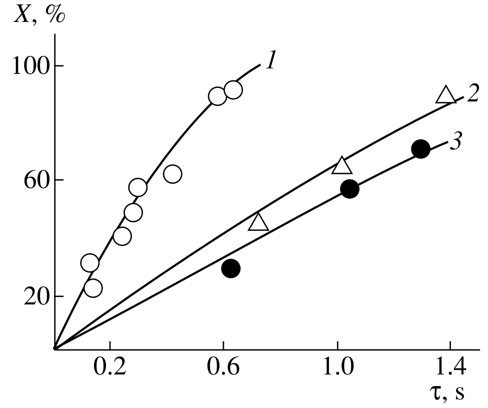

Fig. 1. Dependence of dimethyl disulfide conversion at 200°C on contact time (τ) for (*1*) 5% Co/Al_2O_3, (*2*) 5% Co/C, and (*3*) 5% Co/SiO_2 sulfide catalysts.

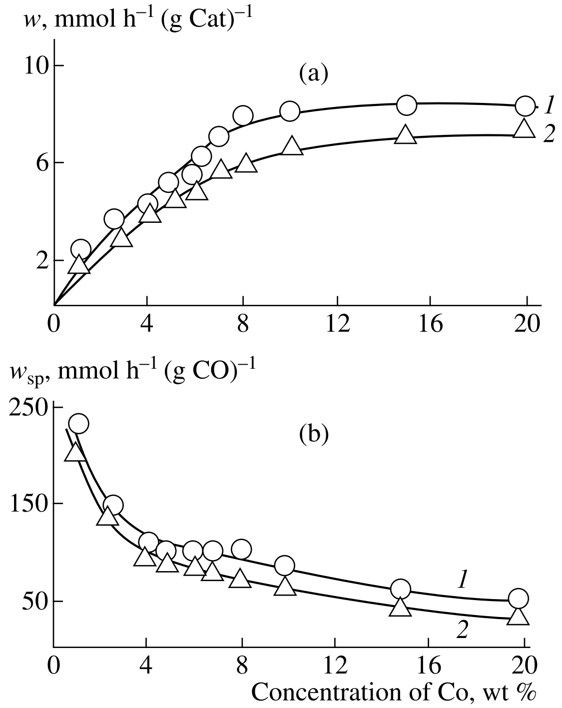

Fig. 2. Dependence of (a) the rate of dimethyl disulfide hydrogenolysis per gram of catalyst and (b) the specific activity at 200°C on Co concentration for Al_2O_3: X = (*1*) 60 or (*2*) 90%.

the catalyst volume and the gas flow rate. Based on the results of analysis, the conversion of dimethyl disulfide (X, %), the yields of products (Y, mol %), the selectivity of methanethiol formation (Y/X, %), the rate of dimethyl disulfide transformation at a constant conversion per gram of a catalyst (w, mmol h^{-1} (g Cat)$^{-1}$), the specific activity as the rate of reaction per gram of cobalt (w_{sp}, mmol h^{-1} (g Co)$^{-1}$), and the production of methanethiol (mmol h^{-1} (g Cat)$^{-1}$) were calculated.

RESULTS AND DISCUSSION

The effect of the nature of the support on the activity of cobalt sulfide catalysts was studied using catalysts containing 5 wt % Co on Al_2O_3, SiO_2, and a carbon support as examples. These catalysts were treated with a mixture of hydrogen sulfide with helium at $T = 250$°C and with hydrogen at $T = 200$°C. The experiments were performed at $T = 200$°C, an initial dimethyl disulfide concentration (C_0) of 1.8 vol %, and various τ. In the presence of the test cobalt catalysts, the hydrogenolysis of dimethyl disulfide to methanethiol primarily occurred:

$$CH_3SSCH_3 + H_2 = 2CH_3SH.$$

This reaction was accompanied by the formation of small amounts of dimethyl sulfide and H_2S because of the condensation of methanethiol

$$2CH_3SH \rightleftarrows (CH_3)_2S + H_2S.$$

The yields of by-products (dimethyl sulfide and H_2S) on CoS/Al_2O_3 and CoS/C at $X \geq 90$ mol % varied from 1 to 4 mol %, whereas the yield of dimethyl sulfide on CoS/SiO_2 even at $X = 60$% was 1 mol %.[1]

Cobalt sulfide catalysts based on Al_2O_3 were much more active (by a factor of 2.5–3) than cobalt sulfide on SiO_2 or the carbon support (Fig. 1). Therefore, the reaction in the presence of cobalt sulfide supported on aluminum oxide was studied in more detail.

Before experiments, the catalysts containing 1–20 wt % Co on Al_2O_3 were treated with a mixture of $H_2S + H_2$ at 250°C and then with hydrogen at 200°C. The experiments were performed on each catalyst at $T = 200$°C, $C_0 = 1.6 \pm 0.1$ vol %, and various τ. As can be seen in Table 1, the conversion of dimethyl disulfide and the yield of methanethiol increased with contact time; an amount of dimethyl sulfide was formed at longer contact times. The yield of dimethyl sulfide decreased as the concentration of cobalt was increased, and the yield of dimethyl sulfide on catalysts containing more that 10 wt % cobalt was no higher than 0.3% even at a dimethyl disulfide conversion of about 96%. The yield of dimethyl sulfide increased to 2.5–5.0 mol % when the value of τ was greater than the time taken to reach 100% conversion.

To compare quantitatively the activities of catalysts with various cobalt sulfide contents, we found the rates of dimethyl disulfide conversion per gram of a catalyst and per gram of Co at X = 60 and 90% from kinetic curves. As can be seen in Fig. 2, the value of w increased as the Co content was increased from 1 to 8 wt % and remained unchanged at higher cobalt concentrations. The specific activity dramatically decreased as the Co content was increased from 1 to 6 wt %; then, the decrease of w_{sp} slowed down. This

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[1] Henceforth, only the yield of dimethyl sulfide is specified; it was equal to the yield of H_2S to within the experimental error.

Table 1. Hydrogenolysis of dimethyl disulfide in the presence of sulfide catalysts with various cobalt concentrations on Al_2O_3

Concentration of Co, wt %	τ, s	*X*, %	Yield, mol %		Concentration of Co, wt %	τ, s	*X*, %	Yield, mol %	
			methanethiol	dimethyl sulfide				methanethiol	dimethyl sulfide
1.0	0.40	40	40	0	7.0	0.15	33	32	0
	0.54	61	60	0		0.30	69	69	0
	0.85	75	76	0		0.44	95	94	0.3
2.5	0.30	42	42	0	8.0	0.15	50	50	0
	0.61	84	83	0.3		0.35	83	79	1.2
	0.91	98	93	2.0		0.47	100	96	2.5
4.0	0.27	30	31	0	10.0	0.16	45	45	0
	0.43	53	54	0		0.21	60	57	0
	0.57	73	69	0		0.44	96	95	0.3
5.0	0.26	41	39	0	15.0	0.14	43	41	0
	0.32	57	54	0		0.29	80	81	0
	0.67	95	87	4		0.46	93	93	0.3
6.0	0.26	40	40	0	20	0.17	63	57	0
	0.43	70	68	0		0.30	87	82	0
	0.54	83	78	0		0.36	96	90	0.2

Note: $T = 200°C$; $C_0 = 1.6 \pm 0.1$ vol %.

decrease was likely due to a change in the dispersity of the active component.

The hydrogenolysis of dimethyl disulfide at T = 180–260°C was studied in the presence of an 8% Co/Al_2O_3 sulfide catalyst presulfurized at 400°C and additionally reduced at an experiment temperature. According to data in Table 2, an increase in the contact time at a constant temperature resulted in an increase in the conversion of dimethyl disulfide and in the yields of products. Methanethiol was the main product, and dimethyl sulfide was also formed under certain conditions. At T = 180°C, dimethyl sulfide was not detected even at X = 90%; it appeared at higher temperatures, and its yield increased with hydrogenolysis temperature and contact time, which facilitated methanethiol condensation [9]. As follows from Fig. 3, a high yield of dimethyl sulfide at T = 250°C was reached at a contact time shorter than that at T = 190°C by a factor of ~7. At T = 250–260°C, hydrogenolysis also occurred with C–S bond cleavage in dimethyl disulfide; as a result of this, methane and H_2S were formed in ~1 mol % yield.

In the presence of the 8% Co/Al_2O_3 sulfide catalyst, the values of $\log(1/1 - X)$ linearly increased with τ at various temperatures (Fig. 4). This suggests the occurrence of dimethyl disulfide hydrogenolysis as a first-order reaction. From the dependence of the logarithm of the first-order rate constant on $1/T$ (Fig. 5), it follows that the apparent activation energy of dimethyl disulfide hydrogenolysis is equal to 79 ± 5 kJ/mol.

The experimental results suggest that a catalyst with a high concentration of cobalt sulfide on Al_2O_3 (7–20 wt % Co) prepared by the treatment of cobalt chloride supported on Al_2O_3 with a mixture of $H_2S + H_2$ at T = 400°C should be used for performing a productive and selective process of the hydrogenolysis of dimethyl disulfide to methanethiol. The reaction should be performed at T = 200–260°C and dimethyl disulfide conversion to 90–95%.

We compared the results of dimethyl disulfide hydrogenolysis on CoS/Al_2O_3 and other sulfide catalysts studied previously [2]. We found that, under identical conditions, for example, at T = 200°C and X = 50%, the CoS/Al_2O_3 catalyst was superior to Ru, Mo, and Ni sulfides supported on Al_2O_3 or Pd and W sulfides in specific activity by a factor of 1.5–2 or 6–15, respectively. Its specific activity was approximately half of that of the most active rhodium sulfide catalyst.

Table 2. Hydrogenolysis of dimethyl disulfide on an 8% Co/Al_2O_3 catalyst at various temperatures

T, °C	τ, s	X, %	Yield, mol %		T, °C	τ, s	X, %	Yield, mol %	
			methanethiol	dimethyl sulfide				methanethiol	dimethyl sulfide
180	0.23	24	24	0	220	0.05	43	43	0
	0.49	60	61	0		0.12	80	80	0
	0.66	90	89	0		0.23	96	90	2.6
190	0.34	57	54	0	240	0.06	60	56	1.4
	0.59	79	76	0		0.11	90	83	3.0
	0.74	90	84	3.0		0.18	94	77	5.3
200	0.15	67	66	0	250	0.02	49	50	0
	0.23	80	77	0.4		0.05	85	83	0.3
	0.33	91	88	1.3		0.11	98	91	3.7
210	0.05	46	47	0	260	0.02	61	58	0.2
	0.12	79	80	0		0.03	76	73	0.2
	0.18	87	82	0.3		0.07	98	88	3.5

At the same time, as can be seen in Table 3, the productivity of our samples in terms of methanethiol was higher than the values obtained on sulfurized cobalt oxide [7, 8] and rhodium sulfide catalysts [2].

It is likely that an enhanced activity of cobalt sulfide catalysts is due to the fact that CoS readily undergoes partial reduction. Indeed, the temperature of catalyst activation affects the activity of cobalt sulfide catalysts. This was found using a 7% Co/Al_2O_3 catalyst as an example, which was treated with a mixture of $H_2S + H_2$ for 1 h at various temperatures and then with hydrogen at 200°C for 0.5 h before activity measurements. It can be seen in Table 4 that, as the temperature of sulfurization was increased from 200 to 400°C, the rate of dimethyl disulfide hydrogenation (for example, at $X = 70\%$) somewhat increased, whereas the value of w decreased at higher sulfurization temperatures. The partial reduction of transition metal sulfides after the thermal treatment of them with a mixture of $H_2S + H_2$ has been reported in a number of publications. Thus, Mashkina

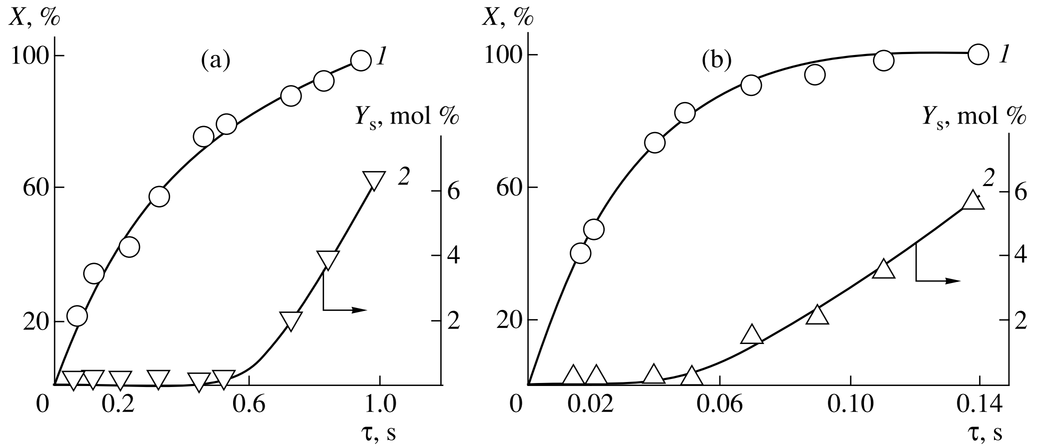

Fig. 3. Dependence of (*1*) dimethyl disulfide conversion and (*2*) dimethyl sulfide yield on contact time in the presence of an 8% Co/Al_2O_3 sulfide catalyst at T = (a) 190 and (b) 250°C.

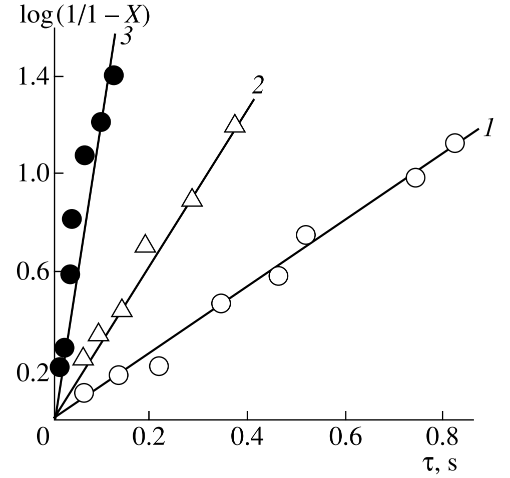

Fig. 4. Dependence of $\log(1/1 - X)$ on contact time in the reaction of dimethyl disulfide hydrogenolysis on an 8% Co/Al_2O_3 sulfide catalyst at T = (*1*) 190, (*2*) 210, and (*3*) 250°C.

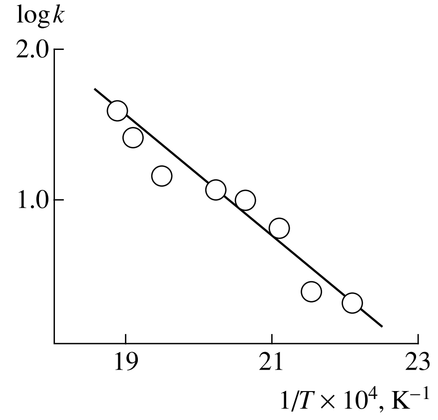

Fig. 5. Arrhenius plot of the rate constant of dimethyl disulfide hydrogenolysis on an 8% Co/Al_2O_3 catalyst.

et al. [10] found that, after the treatment of cobalt sulfide with a mixture of 15% H_2S + 85% H_2 at 400°C, it lost an amount of sulfur. As in the case with other metal sulfides, coordinatively unsaturated cations appeared in this case. It is believed that dimethyl disulfide is coordinated to the Co cation with the participation of a sulfur atom followed by the cleavage of the S–S bond and the formation of surface thiolates. These thiolates react with hydrogen atoms to form methanethiol.

The concentration of coordinatively unsaturated cations on the surface increased after the treatment of a Co catalyst with a mixture of $H_2S + H_2$ at $T > 400$°C. This was favorable for not only the hydrogenolysis of dimethyl disulfide with the formation of methanethiol but also the occurrence of a side reaction of methanethiol condensation [9]. Indeed, as can be seen in Table 4, the formation of by-products on a catalyst sample treated with a mixture of $H_2S + H_2$ at $T > 400$°C was observed

Table 3. Performance characteristics of the process of dimethyl disulfide hydrogenolysis in the presence of sulfide catalysts

Catalyst	T, °C	τ, s	X, %	Selectivity of methanethiol formation, %	Productivity, mmol methanethiol h^{-1} (g Cat)$^{-1}$
2.4% Co/Al_2O_3 [7, 8]	200	0.06	41	13.4	3.3
5% Rh/Al_2O_3 [2]	200	0.39	96	94	11.1
	220	0.29	93	91	14.0
	240	0.18	78	88	18.4
	260	0.14	94	87	28.2
8% Co/Al_2O_3	200	0.14	67	98.5	16.4
(this work)	200	0.30	91	96.7	10.2
	210	0.26	90	95.6	11.5
	220	0.21	96	93.8	14.9
	240	0.08	75	93.3	93.3
	250	0.07	92	95.6	46.0
	260	0.06	98	91.8	49.6
	260	0.03	67	94	81.1

Table 4. Effect of the sulfurization temperature of a 7% Co/Al_2O_3 sulfide catalyst on its activity in the hydrogenolysis on dimethyl disulfide

T, °C*	τ, s	X, %	Yield, mol %		w^{**}, mmol h^{-1} (g Cat)$^{-1}$
			methanethiol	dimethyl sulfide	
200	0.18	51	49	0	7.2
	0.36	84	84	0	
250	0.20	56	53	0	7.0
	0.38	86	87	0	
350	0.19	66	66	0	7.5
	0.39	90	86	0	
375	0.19	57	54	0	7.8
	0.40	93	84	2.0	
400	0.18	72	68	0	10.8
	0.39	98	94	2.0	
450	0.19	65	62	0.3	8.1
	0.40	90	80	3.0	

Note: $T = 200$°C; $C_0 = 1.6$ vol %.

* The temperature of catalyst treatment with 15% H_2S + 85% H_2.

** At $X = 70$%.

even at a relatively low conversion of dimethyl disulfide.

In conclusion, note that, in the process of methanethiol production from dimethyl disulfide, the CoS/Al_2O_3 catalyst is superior to other known catalytic systems in activity and selectivity.

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