Activity of Cobalt Sulfide Catalysts in the Hydrogenolysis of Dimethyl Disulfide to Methanethiol: Effects of the Nature of a Support and the Procedure of Supporting a Cobalt Precursor

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Abstract—The conversion of dimethyl disulfide to methanethiol on various catalysts containing supported cobalt sulfide in an atmosphere of hydrogen was studied at atmospheric pressure and $T = 190°C$. On CoS introduced into the channels of zeolite HSZM-5, the process occurred at a high rate but with a low selectivity for methanethiol because the proton centers of the support participated in a side reaction with the formation of dimethyl sulfide and hydrogen sulfide. Under the action of sulfide catalysts supported onto a carbon support, aluminum oxide, silicon dioxide, and an amorphous aluminosilicate, the decomposition of dimethyl disulfide to methanethiol occurred with 95–100% selectivity. The CoS/Al_2O_3 catalysts were found to be most efficient. The specific activity of alumina–cobalt sulfide catalysts only slightly depended on the phase composition and specific surface area of Al_2O_3. The conditions of the thermal treatment and sulfurization of catalysts and, particularly, the procedure of supporting a cobalt precursor onto the support were of key importance. Catalysts prepared through the stage of supporting nanodispersed cobalt hydroxide were much more active than the catalysts based on supported cobalt salts.

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INTRODUCTION

It is well known [1] that cobalt sulfide catalysts are most efficient in the production of alkanethiols by the hydrogenolysis of readily available dialkyl disulfides. For example, a 5% Co/Al_2O_3 sulfide catalyst prepared by the impregnation of aluminum oxide with an aqueous solution of cobalt chloride accelerated the hydrogenolysis of diethyl disulfide: at $T = 250°C$, $P = 0.1$ MPa, and 90% conversion of the disulfide, the yield of ethanethiol was 54 mol %; hydrogen sulfide, diethyl sulfide, and ethylene were formed as by-products [2]. On a 2.4% Co/Al_2O_3 catalyst, which was prepared by the impregnation of aluminum oxide with an aqueous solution of cobalt nitrate followed by drying, calcination in air, and sulfurization, the hydrogenolysis of dimethyl disulfide (DMDS) at $T = 200°C$, $P = 0.1$ MPa, and an H_2/DMDS molar ratio of 2 : 1 occurred with a selectivity for methanethiol formation of no higher than 50% [3, 4]. Dimethyl sulfide and hydrogen sulfide were also formed in considerable amounts under the specified conditions. Previously [5, 6], better results were obtained in the hydrogenolysis of DMDS in the presence of cobalt sulfide catalysts prepared by the impregnation of aluminum oxide with cobalt chloride and subjected to thermal treatment and sulfurization. At $T = 180–260°C$ and $P = 0.1$ MPa, DMDS decomposed in the presence of 1–20% Co/Al_2O_3 catalysts to form mainly methanethiol: at a DMDS conversion to 90%, the selectivity of methanethiol formation was close to

100%, and the selectivity somewhat decreased under more severe conditions (a longer contact time and a high temperature) because of methanethiol condensation to dimethyl sulfide. It was noted that the supporting of cobalt chloride onto aluminum oxide resulted in a higher conversion of DMDS than with the use of active carbon or silicon dioxide as supports. However, the effects of the type and structure of supports, the nature of cobalt precursors, and the procedure of supporting these precursors onto the supports have not been studied systematically.

The aim of this work was to find an active and selective catalyst for the hydrogenolysis of DMDS to produce methanethiol. Cobalt sulfide catalysts prepared with the use of various supports and procedures for supporting cobalt precursors were studied.

EXPERIMENTAL

The catalysts were prepared by the incipient wetness impregnation of supports with aqueous solutions of corresponding cobalt compounds using two methods.

Method I. γ-Al_2O_3 ($S_{sp} = 210$ m²/g), γ-Al_2O_3 + 30% χ-Al_2O_3 ($S_{sp} = 236$ m²/g), silicon dioxide ($S_{sp} = 310$ m²/g), a Sibunit (C) carbon support ($S_{sp} = 560$ m²/g), and an amorphous aluminosilicate containing 10% Al (AlSi) ($S_{sp} = 360$ m²/g) were used as catalyst supports. The supports were impregnated with aqueous solutions of cobalt chloride, cobalt nitrate, and

cobalt acetate and dried in air at room temperature for 16 h and then at 110–120°C for 5 h; some samples were calcined at 400–500°C. Uncalcined samples contained cobalt chloride, cobalt nitrate, or cobalt acetate on the surfaces, whereas calcined samples contained cobalt oxide.

Method II. Cobalt catalysts were prepared based on aluminum oxide and zeolite. To obtain Co/Al_2O_3, the supports γ-Al_2O_3 (S_{sp} = 288 m²/g), η-Al_2O_3 (S_{sp} = 245 m²/g), and δ-Al_2O_3 (S_{sp} = 82 m²/g) were incipient wetness impregnated with an aqueous solution of cobalt nitrate and dried in air for 16 h. Thereafter, the samples were treated with an aqueous ammonia solution with pH 9.0, filtered off, washed with distilled water, and dried initially in air at room temperature and then at 110°C for 16 h.

To prepare a cobalt–zeolite catalyst, high-silica zeolite HZSM-5 in the hydrogen form with the atomic ratio Si/Al = 17 was used with no binder (the total aluminum content was 2.15 wt %; sodium and iron impurity concentrations were 0.05 and 0.09 wt %, respectively). Before impregnation, the zeolite was calcined at 300°C to constant weight. Cobalt cations were introduced by the incipient wetness impregnation of the zeolite with an aqueous solution of cobalt chloride at room temperature. The sample was dried in air for 16 h, treated with an aqueous ammonia solution with pH 9.0, filtered off, and washed with distilled water. Thereafter, the catalyst was kept in air to a dry state and then heated at 110°C in air for 6 h. Cobalt occurred in these samples as a hydroxide. After drying, the samples were calcined in air at 250, 350, and 450°C for 6 h at each particular temperature. Nanodispersed cobalt oxide occurred in the calcined samples. The powder was pelletized and crushed, and a fraction of 0.25–0.5 mm was taken. The cobalt contents of all of the catalysts are given in wt % with respect to the support (on a metal basis).

The structures of alumina supports and cobalt-containing samples were studied on a D-8 diffractometer (Bruker) using CuK_α radiation. A reflected-beam graphite monochromator was used to filter off CuK_β radiation. The measurements were performed by scanning with a step of 0.05° and an acquisition time of 15–20 s in the angle region of 2θ = 5°–70°. The size of cobalt-containing particles supported by method II onto structurally different alumina supports was determined from small-angle X-ray scattering data. The particle diameter distribution functions were calculated assuming a spherical shape analogously to a published procedure [7]. The procedure used in this work allowed us to study particle size distributions over the range 0.6–30.0 nm. X-ray diffraction data were used for determining the size of coarser cobalt particles, and these data were processed using the standard Selyakov–Scherrer procedure.

The experiments on the conversion of DMDS were performed at T = 190°C and atmospheric pressure in a flow setup coupled to a chromatograph. Hydrogen from a gas cylinder was supplied to a thermostated saturator filled with DMDS; then, the gas arrived at a heated reactor with a catalyst. A fresh catalyst sample with a grain size of 0.25–0.5 mm was used in each particular experiment. The catalyst was loaded in the reactor and treated with a mixture of 15% H_2S + 85% H_2 at a specified temperature for 1 h and then purged with hydrogen at 190°C for 0.5 h before activity measurements. The experiments were also performed with catalysts that were reduced with hydrogen at 400°C for 1 h but not sulfurized. After activating the catalyst, a mixture of DMDS with hydrogen (the initial concentration of DMDS in hydrogen was 1.6 ± 0.2 vol %) was passed through the catalyst at 190°C. The starting mixture and reaction products were sampled for analysis at regular intervals 0.5 h after supplying the mixture to the reactor. The analysis was performed on an LKhM-8MD chromatograph with a katharometer (a column (2 m × 3 mm) packed with Porapak Q and Porapak R (1 : 1); helium was a carrier gas). The accuracy of analysis was ±5 rel %.

The ratio of the catalyst volume (cm³) to the gas flow rate (cm³/s) at room temperature and atmospheric pressure was taken as the contact time (τ, s). The contact time was changed by varying the catalyst volume and the gas flow rate. Based on the results of analysis, the conversion of DMDS (x, %), the yields of reaction products (y, mol %), the selectivity (S, %) equal to the y/x ratio, and the rate of reaction at x = 60% per gram of the catalyst (w, mmol h⁻¹ (g Cat)⁻¹) were calculated.

RESULTS AND DISCUSSION

In this work, we studied the effect of contact time on the conversion of DMDS, the yields of products, and the selectivity in the presence of sulfide catalysts containing 5 wt % cobalt on various supports: SiO_2, C, Al_2O_3, AlSi, and HZSM-5. The CoHZSM-5 catalyst prepared by method II was treated with a mixture of H_2S + H_2 at 190°C before measuring its activity. The sulfurization of the other catalysts prepared by method I was performed at 400°C. Table 1 summarizes experimental results.

We found that the selective conversion of DMDS occurred on Co/SiO_2, Co/C, and Co/Al_2O_3 sulfide catalysts at various contact times: for the most part, the reaction products contained only methanethiol. By-products (dimethyl sulfide and H_2S) were also formed at DMDS conversions higher than 95%, which were reached at longer contact times; however, the yield of the by-products was no higher than 1 mol %. The selectivity for methanethiol was 95–100% depending on DMDS conversion. The yields of dimethyl sulfide and H_2S on the 5% Co/AlSi catalyst were 0.5–1.6 mol %, and these compounds were formed in detectable amounts even at x > 60%.

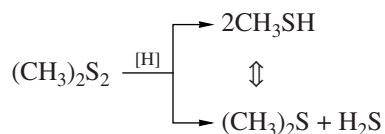On CoHZSM-5 samples, the yield of methanethiol was much lower and the yields of dimethyl sulfide and

Table 1. Effect of contact time on the conversion of dimethyl disulfide and the selectivity of product formation in the presence of cobalt sulfide supported on various supports

Catalyst	τ, s	X, %	y, mol %		S, %	
			methanethiol	dimethyl sulfide	methanethiol	dimethyl sulfide
5% Co/SiO$_2$	0.82	33	33	0	100	0
	1.30	50	49	0	98	0
	1.70	71	70	0	99	0
	2.30	97	95	0.1	98	0.1
5% Co/C	0.80	28	28	0	100	0
	1.40	58	57	0	98	0
	1.80	69	67	0	97	0
	2.50	92	90	0.1	98	0.1
5% Co/Al$_2$O$_3$*	0.25	38	30	0.1	95	0.1
	0.46	68	67	0.4	99	0.6
	0.61	85	83	0.6	98	0.7
	0.67	97	95	0.8	98	0.8
5% Co/AlSi	0.29	39	38	0.1	97	0.3
	0.52	65	64	0.5	98	0.8
	0.71	76	75	0.7	98	0.9
	1.30	98	94	1.9	96	1.9
5% CoHZSM-5**	0.23	44	16	22	36	46
	0.53	67	23	29	34	43
	0.76	73	23	33	32	48
	1.45	94	24	41	26	44

 * Support: γ-Al$_2$O$_3$ + χ-Al$_2$O$_3$.
** The catalyst was prepared by method II; the other catalysts were prepared by method I.

H$_2$S were higher than those on cobalt catalysts based on SiO$_2$, AlSi, C, and Al$_2$O$_3$. The yield of methanethiol changed only slightly as the contact time was increased, whereas the yields of dimethyl sulfide and H$_2$S increased. As the conversion of DMDS was increased to ~75%, the selectivity for methanethiol and H$_2$S remained unchanged. However, at higher DMDS conversions, a decrease in the selectivity for methanethiol and an increase in the selectivity for H$_2$S were observed, whereas the selectivity of dimethyl sulfide formation remained almost constant at various degrees of DMDS conversion. These results allowed us to conclude that the reaction products are formed from DMDS on CoHZSM-5 catalysts via independent reaction paths:

$$(CH_3)_2S_2 \xrightarrow{[H]} \begin{cases} 2CH_3SH \\ \updownarrow \\ (CH_3)_2S + H_2S \end{cases}$$

Under all conditions, the yield of H$_2$S and the selectivity of H$_2$S formation were lower than the corresponding values for dimethyl sulfide; this can be due to its consumption in the course of the reaction.

The activities of cobalt sulfide catalysts on various supports were compared by comparing the overall conversion rates of DMDS found at a DMDS conversion of 60%. As can be seen in Table 2, the Co/AlSi and CoHZSM-5 sulfide catalysts exhibited maximum activities. The other catalysts were less active: Co/Al$_2$O$_3$ by a factor of 1.2–1.4 and Co/SiO$_2$ and Co/C by a factor of

Table 2. Rate of dimethyl disulfide conversion and the selectivity of reaction product formation (at $X = 60\%$) on pure and cobalt sulfide–modified supports

Catalyst or support	w, mmol h^{-1} (g Cat)$^{-1}$	S, %		
		methanethiol	dimethyl sulfide	H$_2$S
5% Co/SiO$_2$	1.8	100	<0.4	0
SiO$_2$	0.1	70	0	0
5% Co/C	1.9	100	0	0
C	<0.02	–	0	0
5% Co/Al$_2$O$_3$*	4.2	100	<0.4	0
Al$_2$O$_3$*	1.6	30	51	17
5% Co/AlSi	5.0	99	0.4	0
AlSi	0.4	65	16	12
5% CoHZSM-5**	5.7	35	40	22
HZSM-5	5.6	22	52	20

 * Support: γ-Al$_2$O$_3$ + χ-Al$_2$O$_3$.
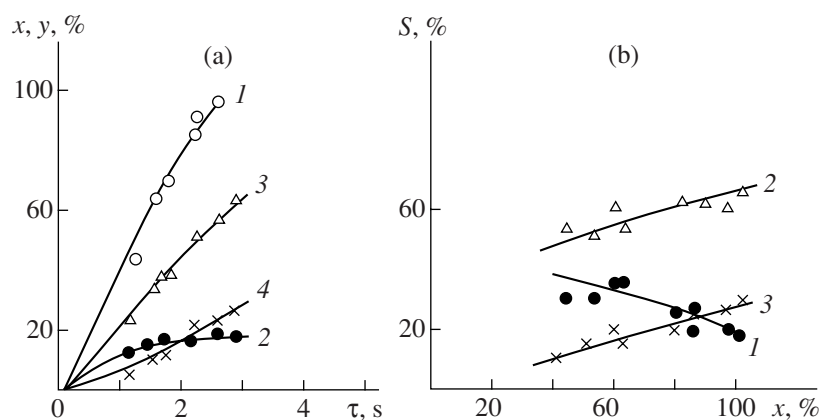** The catalyst was prepared by method II; the other cobalt catalysts were prepared by method I.

Fig. 1. (a) Effect of contact time on (*1*) dimethyl disulfide conversion and the yields of (*2*) methanethiol, (*3*) dimethyl sulfide, and (*4*) H$_2$S. (b) Dependence of the selectivity of (*1*) methanethiol, (*2*) dimethyl sulfide, or (*3*) H$_2$S formation on dimethyl disulfide conversion. Catalyst: γ-Al$_2$O$_3$ + χ-Al$_2$O$_3$.

~3. The selectivity of methanethiol formation on CoS supported on SiO$_2$, AlSi, C, and Al$_2$O$_3$ at $x = 60\%$ was no lower than 99%, and dimethyl sulfide and H$_2$S were absent from the reaction products. On the cobalt–zeolite catalyst, methanethiol and dimethyl sulfide were formed with close selectivities (35–40%, see Table 2).

To determine the support effect on the apparent activity of cobalt sulfide catalysts, we performed experiments on the conversion of DMDS in an atmosphere of hydrogen at $T = 190°C$ on SiO$_2$, C, AlSi, Al$_2$O$_3$, and HZSM-5 samples that were preactivated under the same conditions as the cobalt sulfide catalysts. The conversion of DMDS almost did not occur on the carbon support and SiO$_2$. The reaction did occur on AlSi but at a very low rate. Thus, we can conclude that, on cobalt catalysts with the use of the above supports, the reaction occurred only on cobalt sulfide. However, Al$_2$O$_3$ and HZSM-5 supports exhibited high activity in the decomposition of DMDS (Table 2).

The conversion of DMDS on aluminum oxide containing no cobalt occurred with the formation of methanethiol, dimethyl sulfide, H$_2$S, and hydrocarbons (ethylene and methane). As the contact time was increased, an increase in the conversion of DMDS and in the yields of products was observed. The selectivity for methanethiol decreased with x, whereas the selectivities for dimethyl sulfide and H$_2$S increased (Fig. 1). It is believed that the decomposition of DMDS on pure Al$_2$O$_3$ to methanethiol occurred with the subsequent methanethiol condensation to dimethyl sulfide. Lower yields of H$_2$S and selectivities for H$_2$S, as compared with those for dimethyl sulfide, can be explained by the participation of H$_2$S in surface protonation [2].

From a comparison between data obtained on Al$_2$O$_3$ and Co/Al$_2$O$_3$, it follows (Tables 1, 2 and Fig. 1) that the introduction of 5% Co into aluminum oxide increased the rate of DMDS conversion by a factor of 2.6, dramatically increased the selectivity for methanethiol, and decreased the selectivity for dimethyl sulfide. Thus, the

effect of aluminum oxide on the activity of an alumina–cobalt sulfide catalyst in the formation of methanethiol is negligibly small; it is likely that the reaction occurs on this catalyst with the participation of cobalt sulfide.

It is likely that the mechanism of methanethiol formation from DMDS on catalysts containing cobalt sulfide supported on Al$_2$O$_3$, a carbon support, SiO$_2$, and AlSi in an atmosphere of hydrogen is identical to that on other transition metal sulfides [1, 2, 8]. The reaction occurs through the step of surface complex formation with the participation of cobalt ions and a sulfur atom of DMDS followed by S–S bond rupture and the formation of CH$_3$S fragments on the surface. Methanethiol is formed by the interaction of these fragments with hydrogen activated at the metal ion. On Co/AlSi, proton centers available on the support surface also participate in the process to result in the occurrence of a side reaction of dimethyl sulfide formation.

The formation of dimethyl sulfide is considerably facilitated in the case of introducing CoS into HZSM-5, which exhibits a higher acidity. It was found that changes in the selectivities of product formation on the zeolite containing no cobalt under varying DMDS conversion were analogous to those observed on CoHZSM-5. However, the selectivity for methanethiol on the cobalt–zeolite catalyst was higher than that on the pure support by a factor of 1.6, whereas the selectivity for dimethyl sulfide was lower by a factor of 1.2. In this case, the rates of DMDS conversion on the catalyst and the support were equal (Table 2, Fig. 2). We can conclude that the support plays the main role in the activity of the CoHZSM-5 sulfide catalyst, whereas the presence of CoS in the catalyst facilitates the direction of the reaction toward a somewhat greater formation of methanethiol with a decrease in the yield of dimethyl sulfide.

In the presence of acid catalysts, the decomposition of DMDS to methanethiol is a heterolytic process [1, 2]. In the contact of DMDS with the catalyst, a complex
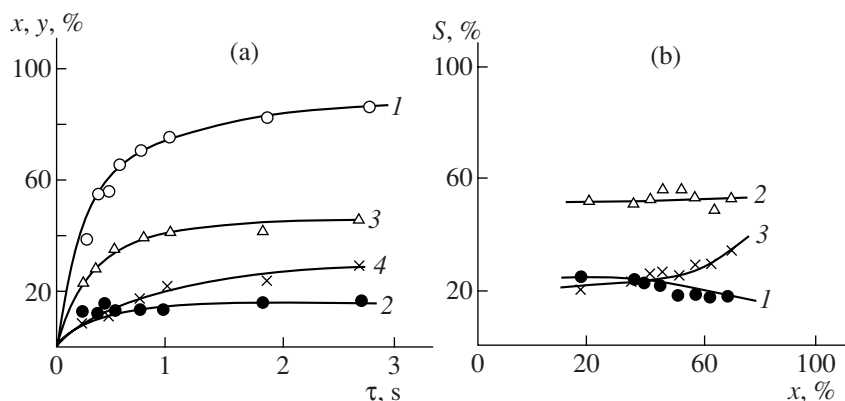
Fig. 2. (a) Dependence of (*1*) dimethyl disulfide conversion and the yields of (*2*) methanethiol, (*3*) dimethyl sulfide, and (*4*) H₂S on contact time. (b) Effect of dimethyl disulfide conversion on the selectivity of (*1*) methanethiol, (*2*) dimethyl sulfide, or (*3*) H₂S formation. Catalyst: HZSM-5.

is formed with the participation of an acid site and a sulfur atom of the substrate followed by decomposition at the S–S bond and the formation of CH_3S structures, which react with protons to result in methanethiol. A portion of the resulting methanethiolate structures (probably with the participation of the acid–base pair of surface sites) undergoes decomposition at the C–S bond at an elevated temperature [9] with the formation of sulfur atoms and CH_3 fragments on the surface. As a result of the reaction of these fragments with the CH_3S structures, dimethyl sulfide is formed, whereas the reaction of protons with sulfur atoms affords H_2S. Proton sites on the surface are mainly restored because of the dissociative chemisorption of H_2S.

Proton and Lewis acid sites (Al^{3+} in a tetrahedral oxygen environment) occur in the channels and on the surface of the parent zeolite HZSM-5. The introduction of cobalt into the zeolite results in the disappearance of Lewis acid sites related to the presence of Al^{3+} and in a partial suppression of proton sites [10]. Both proton and Lewis acid sites can participate in the decomposition of DMDS. In the case of CoHZSM-5, the process can occur under the action of residual proton sites in the zeolite and at Co^{2+} ions, which participate in the activation of both DMDS and hydrogen. A decrease in the concentration of proton sites upon the introduction of cobalt into the zeolite [10] resulted in a decrease in the rate of dimethyl sulfide formation but in an increase in the rate of methanethiol formation. However, the selectivity of methanethiol formation was low. Therefore, the sulfide cobalt-containing zeolite catalyst cannot be considered promising for the production of methanethiol from DMDS, although a high reaction rate was reached in the presence of this catalyst.

Cobalt sulfide supported on aluminum oxide is most efficient in the process of DMDS hydrogenolysis to methanethiol. Therefore, we studied alumina–cobalt sulfide catalysts in most detail; in particular, we considered the effect of the catalyst preparation procedure on the catalyst activity.

The phase composition of samples, the structure and specific surface area of the support, the nature of the cobalt precursor, the supporting procedure, and the conditions of thermal treatment and sulfurization can affect the catalytic properties of Co/Al_2O_3. Thus, we studied in detail a series of Co/Al_2O_3 catalysts with various parameters (Table 3, Figs. 3, 4).

The γ-Al_2O_3, γ-Al_2O_3 + χ-Al_2O_3, and η-Al_2O_3 supports exhibited close specific surface areas. Cobalt catalysts prepared by the same method based on the above supports did not dramatically differ (to within 20 rel %) in terms of activity. The specific surface area of the δ-Al_2O_3 support was lower than that of γ-Al_2O_3 or η-Al_2O_3 by a factor of about 3. The rate of DMDS hydrogenolysis on Co/δ-Al_2O_3 per gram of the catalyst was lower than that in the case of catalysts based on alumina of the other phase composition. However, cobalt catalysts on the specified supports exhibited close specific activities per unit surface area.
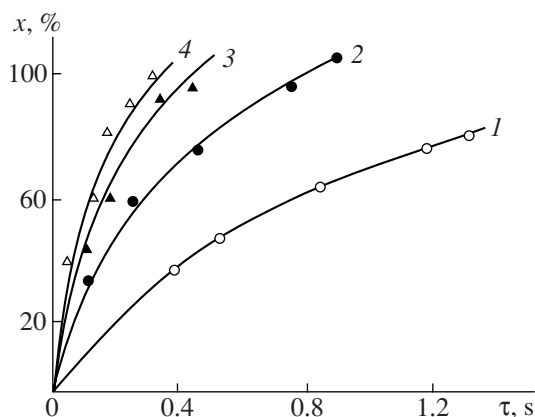

Fig. 3. Dimethyl disulfide conversion on the 10% Co/(γ-Al_2O_3 + χ-Al_2O_3) catalyst prepared from cobalt acetate by method I and sulfurized at T = (*1*) 190 or (*2*) 400°C after drying or calcined at T = 400°C and sulfurized at T = (*3*) 190 or (*4*) 400°C.

Table 3. Dependence of the activity of Co/Al$_2$O$_3$ sulfide catalysts in the conversion of dimethyl disulfide on the nature of the precursor, the phase composition and specific surface area of the support, and the temperature of catalyst activation

Precursor	T, °C		w, mmol h⁻¹ (g Cat)⁻¹ at $x = 60\%$	Precursor	T, °C		w, mmol h⁻¹ (g Cat)⁻¹ at $x = 60\%$
	calcination for 5 h	H$_2$S + H$_2$, 1 h			calcination for 5 h	H$_2$S + H$_2$, 1 h	
2.5% Co/γ-Al$_2$O$_3$ (method I)				10% Co/(γ + χ)-Al$_2$O$_3$ (method I)			
CoCl$_2$	–	–*	1.3	CoCl$_2$	–	400	5.3
	–	400	4.6	Co(C$_2$H$_3$O$_2$)$_2$	–	190	2.2
	400	400	5.2		–	400	6.2
	500	400	2.0		400	190	7.5
Co(NO$_3$)$_2$	500	–*	2.8		400	400	9.2
	400	400	3.9	10% Co/γ-Al$_2$O$_3$			
	500	400	4.3	CoCl$_2$ (method I)	–	400	6.2
Co(C$_2$H$_3$O$_2$)$_2$	–	400	5.5		–	190	4.0
8% Co/(γ + χ)-Al$_2$O$_3$ (method I)				Co(NO$_3$)$_2$ (method II)	–	–*	8.8
CoCl$_2$	–	400	5.9		–	400	16.2
	–	250	3.6		–	190	17.0
Co(NO$_3$)$_2$	500	400	6.6		–	190**	16.3
	–	400	4.8		–	190***	7.8
					–	400***	5.3

*The catalyst was only reduced with hydrogen at $T = 400°C$.

**Support: η-Al$_2$O$_3$.

***Support: δ-Al$_2$O$_3$.

The aluminum oxides used were essentially different in structure. It is well known [11] that γ-Al$_2$O$_3$ and η-Al$_2$O$_3$ are usually described in terms of a single structural model of nonstoichiometric spinel with different cation distributions over octahedral and tetrahedral positions. Both of these modifications contain cationic vacancies in their structures. However, vacancies in the η-Al$_2$O$_3$ structure mainly occur in octahedral positions, whereas they are equiprobably distributed over octahedral and tetrahedral positions in the γ-Al$_2$O$_3$ structure. These and other structure peculiarities resulted in a tetragonal distortion of the cubic lattice of γ-Al$_2$O$_3$, as

Fig. 4. Dependence of conversion upon contact time on the 10% Co/γ-Al$_2$O$_3$ catalyst prepared from cobalt chloride by method I and sulfurized at $T =$ (1) 190 or (2) 400°C or (3) treated with hydrogen at $T = 400°C$ and unsulfurized.

compared with the lattice of η-Al$_2$O$_3$. The structure of χ-Al$_2$O$_3$ consists of the same building blocks as that of γ-Al$_2$O$_3$ or η-Al$_2$O$_3$; however, the stacking of these building blocks by a microtwinning mechanism results in the appearance of a hexagonal closest packing of anions. The occurrence of a superstructure is characteristic of a high-temperature δ-Al$_2$O$_3$ phase. The unit cell of δ-Al$_2$O$_3$ is considered as tetragonal with the triplication of a cubic lattice spacing, which characterizes γ-Al$_2$O$_3$. However, the test cobalt catalysts prepared by the same method based on various aluminum oxides were comparable in terms of specific activity. Thus, we can conclude that the structure of alumina has no detectable effect on the activity of cobalt catalysts for the hydrogenolysis of DMDS to methanethiol.

The activity of Co/Al$_2$O$_3$ sulfide catalysts depended on the conditions of catalyst activation. The samples based on cobalt chloride and cobalt nitrate subjected only to hydrogen reduction at 400°C were much less active (by a factor of 1.5–3.5) than those treated with a mixture of H$_2$S + H$_2$. The temperature of sample calcination before sulfurization was also of importance for the activity of catalysts. The activity of the Co/Al$_2$O$_3$ sulfide catalysts prepared by method I (the impregnation of a support with cobalt chloride and heating in air at 400°C after drying) and sulfurized with a mixture of H$_2$S + H$_2$ at 400°C was approximately the same as that of the catalysts that were not calcined in air. However, the activity of these samples decreased by a factor of ~2 after thermal treatment at 500°C. At the same time, nitrate and acetate catalysts should be heated at 400–
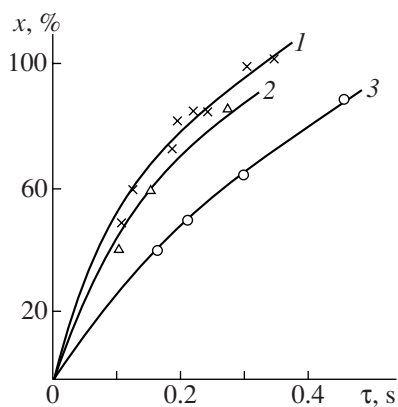
500°C in a flow of air before sulfurization. The samples of Co/(γ-Al$_2$O$_3$ + χ-Al$_2$O$_3$) prepared from cobalt acetate and calcined at 400°C before sulfurization were more active than the samples that were only dried by a factor of 1.5–3.4. The activity of uncalcined catalysts based on cobalt chloride or cobalt acetate (method I) increased by a factor of 1.6–2.8 as the sulfurization temperature was increased from 190–250 to 400°C. In calcined acetate samples, the sulfurization temperature was less important. We found that optimum conditions for the activation of catalysts prepared in accordance with method I were the following: sulfurization at 400°C and calcination of the samples from cobalt nitrate and cobalt acetate at 500°C before sulfurization or no calcination for the samples from cobalt chloride. In the samples prepared using method II, an increase in the sulfurization temperature from 190 to 400°C resulted in a considerable decrease in activity.

From a comparison between the activities of 2.5% Co/Al$_2$O$_3$ catalysts prepared from cobalt salts (method I) and activated under optimum conditions, it follows that the use of cobalt chloride, cobalt nitrate, and cobalt acetate as precursors resulted in insignificant differences. The activity of the 10% Co/Al$_2$O$_3$ catalyst from cobalt acetate was higher than that of an analogous catalyst prepared from cobalt chloride by a factor of 1.4. The procedure of supporting a cobalt precursor onto a support has a great positive effect. Thus, the activity of the sample of 10% Co/Al$_2$O$_3$ prepared with the use of cobalt nitrate, which was further converted into cobalt hydroxide on the surface (method II), was higher by a factor of 1.7–2.6 than that of catalysts prepared by method I with the use of cobalt salts and calcined and sulfurized under optimum conditions. It is most likely that the activity of the catalyst prepared by method II was higher because of the smaller size of cobalt-containing precursor particles on the support surface. Thus, we found that the predominant sizes of cobalt-containing particles supported on γ-Al$_2$O$_3$, η-Al$_2$O$_3$, and δ-Al$_2$O$_3$ were 1.5–2.0 nm for catalysts prepared by method II regardless of the structure and the specific surface area of the support, whereas catalysts prepared by method I contained particles of size 30–40 nm.

Thus, the experimental results allowed us to conclude that it is unreasonable to use cobalt sulfide catalysts containing large amounts of strong proton sites on the surface of supports (such as decationized zeolites) for DMDS hydrogenolysis primarily directed toward the formation of methanethiol because side reactions occur at high rates in the presence of these proton sites to decrease the yield of the target product. Cobalt sulfide catalysts based on silicon dioxide or a carbon support are selective in the formation of methanethiol;

however, they are insufficiently active. Cobalt sulfide supported on aluminum oxide is most efficient. As found previously [8], other transition metal sulfides supported on alumina are also more active in DMDS hydrogenolysis to methanethiol than those supported on silica or carbon. A comparison between the specific activities of various samples demonstrated that this value for a Rh/Al$_2$O$_3$ sulfide catalyst was greater than that for Ru, Mo, and Ni sulfides by a factor of 3–4; for Pd sulfide by a factor of 11; and for W sulfide by a factor of 27. A disadvantage of the rhodium catalyst is that it contains an expensive and rare active component. Mashkina and Khairulina [5] found that the productivity reached in the presence of a sulfide catalyst prepared by supporting cobalt chloride onto Al$_2$O$_3$ under certain conditions was higher than that on a rhodium sulfide catalyst. Thus, the results of this study indicate that the productivity of an alumina–cobalt sulfide catalyst can be increased by a factor of at least 2.5 if γ-Al$_2$O$_3$ with a large specific surface area is used as a support and the catalyst is prepared by supporting a cobalt salt followed by its conversion into a hydroxide. Upon the activation of this hydroxide, a highly dispersed active component is formed in the catalyst.

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