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Selective Hydrogenation of Diethyl Disulfide to Ethanethiol in the Presence of Sulfide Catalysts

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Abstract—The gas-phase reaction of diethyl disulfide hydrogenation at atmospheric pressure in the presence of supported transition metal sulfides was studied. The reaction of diethyl disulfide with hydrogen at $T = 200°C$ resulted in ethanethiol, and the selectivity to ethanethiol was no lower than 94%. The selectivity decreased at a higher temperature because of diethyl disulfide decomposition to ethylene and hydrogen sulfide. The reaction of diethyl disulfide in the presence of hydrogen occurred at a higher rate and selectivity than that in an atmosphere of helium. The activity of metal sulfides supported on aluminum oxide was higher than on the other studied supports—aluminosilicate, silica gel, and a carbon support. Metal sulfides supported on Al_2O_3 were arranged in the following order according to their activity: $Rh > Ru > Mo \geq Pd > Ni > W$. Bimetallic catalysts were less active than monometallic catalysts. The activity of catalysts increased with the sulfide sulfur content; the partial reduction of metal sulfides also increased the catalytic activity.

INTRODUCTION

Lower alkanethiols are used as natural gas odorants and as feedstock for the synthesis of practically important thio compounds. The catalytic decomposition of dialkyl disulfides is a promising method for preparing them. Previously [1, 2], we found that dimethyl disulfide and diethyl disulfide were converted into corresponding alkanethiols on oxide catalysts in an inert atmosphere or in the presence of H_2S. However, the reaction was nonselective, and it was accompanied by side processes of the formation of alkenes, H_2S, dialkyl sulfides, and sulfur. Dialkyl disulfides easily underwent hydrogenolysis in an atmosphere of molecular hydrogen at elevated temperature and pressure in the presence of solid catalysts with the release of H_2S and hydrocarbons; in this case, alkanethiols were formed in trace amounts [3]. The yield of alkanethiols from dialkyl disulfides increased if the hydrogenation was performed under milder conditions. Thus, Cadot *et al.* [4] studied the hydrogenation of dimethyl disulfide at $T = 200°C$, $P = 0.1$ MPa, and an $H_2 : (CH_3)_2S_2$ molar ratio of 2 : 1 in the presence of Ni, Co, and Mo sulfides or bimetallic CoMo, NiMo, and NiW sulfide catalysts supported on Al_2O_3. They found that the selectivity of methanethiol formation was as high as 65%, and it increased on the addition of H_2S or H_2O to the system. The selective hydrogenation of dialkyl disulfides to alkanethiols on other sulfide catalysts was not studied.

This work was devoted to a study of the hydrogenation of diethyl disulfide to ethanethiol on sulfide catalysts with various compositions.

EXPERIMENTAL

Solid supports calcined in air at $T = 500–530°C$ for 5 h were used to prepare supported catalysts (the carbon support Sibunit (C) was calcined in helium at $T = 300°C$). The specific surface areas (m^2/g) of the supports were the following: 200–250 for Al_2O_3, 360 for amorphous aluminosilicate (AlSi) containing 10% Al, 300 for SiO_2, and 560 for C. Monometallic catalysts were prepared by the incipient wetness impregnation of the supports with aqueous salt solutions (Pd, Rh, Ru, and Ni chlorides; ammonium molybdate; ammonium tungstate; and nickel nitrate). To prepare a Pd sample containing *para*-toluenesulfonic acid, Al_2O_3 was impregnated with a $PdCl_2$ solution; the sample was dried and then additionally impregnated with an aqueous *para*-toluenesulfonic acid solution. After impregnation, the samples were held in air for 12 h at room temperature and then dried at $T = 110°C$ for 5 h. After drying, Ni catalysts (2.5 wt % Ni) prepared from nickel nitrate were calcined in a flow of air at 500°C for 5 h. A Pd metal catalyst was prepared by the reduction of supported $PdCl_2$ with hydrogen at $T = 290°C$ for 16 h. Before activity measurements, all samples (unless otherwise specified) were sulfidized with a mixture of 15% H_2S + 85% H_2 at a specified temperature (Pd, Rh, and Ru catalysts, at $T = 150°C$ for 1 h; Ni and W catalysts, at $T = 250$ and 300°C, respectively, for 1 h; and Mo catalysts, at $T = 400°C$ for 2 h), which provided the complete decomposition of supported salts, and reduced with hydrogen at 200°C for 0.5 h. The conversion of diethyl disulfide in a hydrogen atmosphere was also examined in the presence of the supports (Al_2O_3, AlSi, SiO_2, and C), which were treated initially with a mixture of 15% H_2S + 85% H_2 at $T = 400°C$ for 1 h and then in a flow of H_2 at $T = 200°C$ for 0.5 h before activity measurements. Bimetallic NiMo, CoMo, and NiW sulfide catalysts were also prepared by incipient wetness impregnation. The supports were impregnated with solutions containing a mixture of cobalt nitrate or nickel nitrate with ammonium molybdate or ammonium tungstate, held in air at room temperature for 12 h, dried at $T = 110°C$ for 5 h, and calcined in a flow of air at $T = 500°C$ for 5 h (the NiW catalyst was not calcined). Before activity measurements, the samples were sulfidized with a mixture of 15% H_2S + 85% H_2 at $T = 400°C$ for 2 h and then reduced in a flow of H_2 at $T = 300°C$ for 1 h. Bimetallic catalysts were also prepared by the successive impregnation of supports: initially, the supports were impregnated with a nickel (cobalt) nitrate solution; the samples were dried, calcined in a flow of air at $T = 500°C$, and then impregnated with an ammonium molybdate or ammonium tungstate solution; the further thermal treatment was performed as specified above. To prepare a bimetallic PdW catalyst, Pd was supported onto Al_2O_3 from a $PdCl_2$ solution; the sample was dried, then impregnated with an ammonium tungstate solution and dried again. Before use, the sample was sulfidized with a mixture of 15% H_2S + 85% H_2 at $T = 300°C$ for 1 h and reduced in a flow of H_2 at $T = 300°C$ for 0.5 h.

Reagent-grade and chemically pure chemicals were used in this study. The metal and sulfur contents of catalysts were judged from elemental analysis data.

The activity of catalysts was determined in a flow unit at atmospheric pressure. The hydrogenation of diethyl disulfide was performed at $T = 200–350°C$, atmospheric pressure, and the initial diethyl disulfide concentration $C_0 = 1.1–1.3$ vol %. It was found in preliminary experiments with a (2.5 Ni, 10Mo)/Al_2O_3[1] sulfide catalyst as an example that, as the hydrogen content of helium was increased from 5 to 15 vol %, the reaction rate increased in proportion to the H_2 content, and this rate remained almost unchanged at higher hydrogen concentrations. All experiments on the hydrogenating activity of catalysts were performed in pure hydrogen. Hydrogen from a gas cylinder was supplied to a thermostatted bubbler filled with diethyl disulfide; then, the gas arrived at a heated reactor with a catalyst. The samples of hydrogenation products were taken 0.5 h after supplying a mixture to the reactor. The duration of an experiment for determining activity was 1 h. The products were analyzed on an LKhM-8MD chromatograph with a thermal-conductivity detector and a column (2 m × 3 mm) packed with Porapak Q and Porapak R (1 : 1) or 5% XE on Chromaton N AW-DMCS (particle size of 0.20–0.25 mm); helium was used as a carrier gas. A fresh catalyst sample with a particle size of 0.25–0.50 mm was used in each experiment. The ratio of the catalyst volume (cm^3) to the gas-flow rate (cm^3/s) at $T = 20°C$ and $P = 0.1$ MPa was taken as the contact time τ (s). The values of τ were changed by varying the catalyst volume and the gas-flow rate. Based on chemical analysis, the conversion of diethyl disulfide (x, %); the yields of products (y, mol %); the selectivity of ethanethiol formation ($S = y/x$, %); the average specific rate of disulfide conversion at $x = 50\%$ per gram of a catalyst (w_{sp}, mmol (g Cat)$^{-1}$ h^{-1}); and the reaction rate constant, which was taken as a measure of catalytic activity (AKA, l gas (g-atom M)$^{-1}$ s^{-1}, where gas is a flow of a gaseous mixture of diethyl disulfide + H_2, and M is a metal), were calculated.

RESULTS AND DISCUSSION

Diethyl disulfide underwent no reaction in an experiment performed in a reactor filled with 1 ml of broken glass without catalysts at $T = 200–250°C$ and a gas (a mixture of diethyl disulfide + H_2) flow rate of 2 l/h. At $T = 350°C$, the conversion of diethyl disulfide was no higher than 10%, and trace ethanethiol was detected in the reaction products.

The effect of contact time on the conversion of diethyl disulfide and the selectivity of ethanethiol formation was determined in the presence of various catalysts at constant temperature and initial diethyl disulfide concentration in hydrogen. Table 1 summarizes some results. It can be seen that ethanethiol was the main product on all catalysts at $T = 200°C$. The selectivity of its formation was close to 100% at low x; that is, the following reaction occurred:

$$C_2H_5SSC_2H_5 + H_2 = 2C_2H_5SH.$$

Diethyl sulfide, ethylene, and hydrogen sulfide were also present in very small amounts in the reaction products. The selectivity of ethanethiol formation at high diethyl disulfide conversions decreased to ~94% (Table 1, Fig. 1). The supports treated with a mixture of 15% H_2S + 85% H_2 at $T = 400°C$ also accelerated the formation of ethanethiol. The specific rate of diethyl disulfide conversion at $T = 200°C$ in the presence of Al_2O_3, AlSi, SiO_2, or C was 1.4, 0.4, 0.08, and 0.06 mmol (g Cat)$^{-1}$ h^{-1}, respectively. This rate is lower than the rate observed on supported sulfide catalysts by 0.5–2 orders of magnitude. On sulfide catalysts, the reaction of diethyl disulfide hydrogenation was accelerated as the temperature was increased to 250°C; however, the selectivity of ethanethiol formation was lower than that at $T = 200°C$. An increase in the contact time increased the conversion of diethyl disulfide and the yield of ethanethiol to certain limits; the yields of products of deep diethyl disulfide hydrogenation with the release of H_2S and ethylene also increased (Fig. 2).[2] The selectivity of ethanethiol formation decreased with increasing x (Table 1, Fig. 1). At $T = 350°C$, diethyl disulfide primarily decomposed to ethylene and H_2S on all sulfide

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[1] Hereafter, figures before element symbols indicate the element content in wt %.

[2] Figure 2 demonstrates the yield only of H_2S, which was equal to the yield of ethylene.

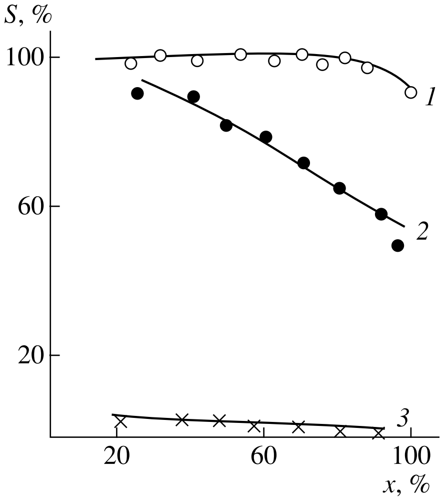


Fig. 1. Selectivity of ethanethiol formation as a function of diethyl disulfide conversion on a $5Pd/Al_2O_3$ sulfide catalyst at T = (*1*) 200, (*2*) 250, or (*3*) 350°C.

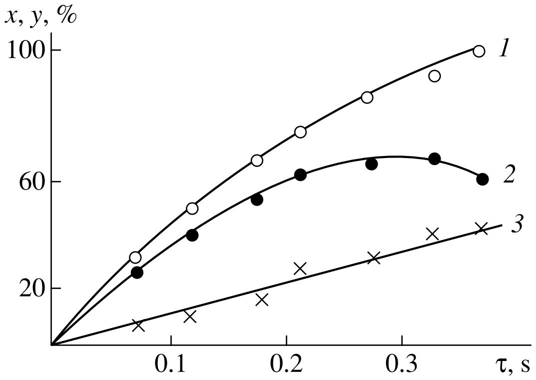


Fig. 2. Effects of contact time on (*1*) diethyl disulfide conversion and the yields of (*2*) ethanethiol and (*3*) H_2S on a $5Mo/Al_2O_3$ sulfide catalyst at T = 250°C.

catalysts, and the selectivity of ethanethiol formation was extremely low (Fig. 1).

The reaction of diethyl disulfide on the used sulfide catalysts also occurred in the absence of hydrogen. In this case, the conversion of diethyl disulfide and the yield of products increased with contact time. In a helium atmosphere, the rate of diethyl disulfide conversion and the selectivity of ethanethiol formation even at low x were much lower than in the presence of hydrogen (Table 2). Moreover, in a helium atmosphere, the activity of catalysts decreased in the course of experiments. In a hydrogen atmosphere, catalysts were stable in operation; for example, the initial activity of Pd and Ru sulfides supported on Al_2O_3 remained unchanged for 3 h.

It was found that the values of $\log(1/1 - x)$ for various sulfide catalysts linearly increased with τ (see, for example, Fig. 3), and a change in the initial diethyl disulfide concentration did not affect the degree of conversion. These results indicate that the hydrogenation of diethyl disulfide is a first-order reaction. The rate constant of the first-order reaction is expressed as k (s^{-1}) = $\frac{1}{\tau}\ln(1/1 - x)$, where $\tau - \frac{V_{Cat}}{V_{gas}}$, V_{Cat} is the catalyst volume, and V_{gas} is the flow rate (l/s) of a gas (a mixture of

Table 1. Effect of contact time on the conversion and selectivity of diethyl disulfide hydrogenation to ethanethiol in the presence of sulfide catalysts

Catalyst	T = 200°C			T = 250°C		
	τ, s	x, %	S, %	τ, s	x, %	S, %
$5Pd/Al_2O_3$	0.19	42	100	0.05	40	90
	0.32	61	98	0.08	60	78
	0.72	88	95	0.14	90	57
$5Rh/Al_2O_3$	0.15	48	99	0.05	49	78
	0.22	66	97	0.07	59	67
	0.44	90	94	0.15	90	50
$5Mo/Al_2O_3$	0.20	44	100	0.12	47	81
	0.36	58	98	0.18	61	79
	0.75	87	93	0.33	88	58
Al_2O_3	1.00	31	90	0.89	44	50
	3.14	68	77	1.50	73	42
	6.50	90	68	1.90	90	35

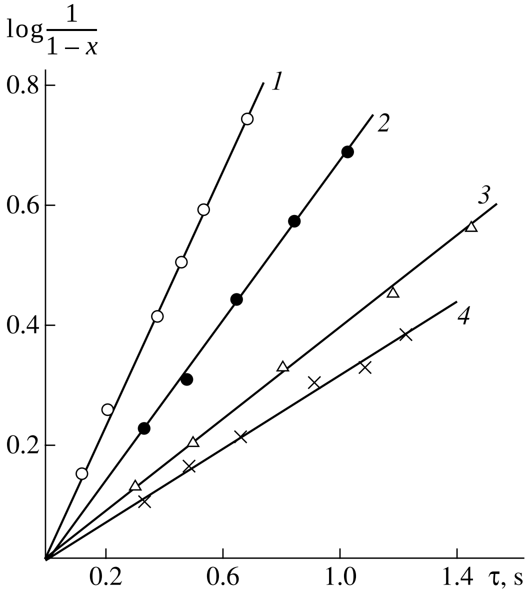


Fig. 3. $\log(1-x)^{-1}$ as a function of contact time in the reaction of diethyl disulfide hydrogenation on sulfide catalysts: (*1*) 5Rh/C, (*2*) $18W/SiO_2$, (*3*) $5Ru/SiO_2$, and (*4*) 10Mo/AlSi.

diethyl disulfide + H_2). The metal constituents of catalysts were different in atomic weights; therefore, the molar concentration of a metal in a given catalyst volume rather than the catalyst volume was taken into account. The above reaction rate constant k in units of l gas (g-atom M)$^{-1}$ s^{-1} was used to compare the catalyst activity (*AKA*) in diethyl disulfide hydrogenation at T = 200°C. Data in Table 3 indicate that the catalyst activity depended on the nature of the metal. For example, sulfide catalysts based on Al_2O_3 were arranged according to the relative *AKA* values in the following order:

M –	Rh >	Ru >	Mo ≥	Pd >	Ni >	W
$k_{rel}, \left(\frac{k_M}{k_w}\right)$ –	4.8	3.1	2.8	2.7	1.7	1.0

Of the test catalysts, a Rh sulfide catalyst was most active; the activity of Ru, Mo, and Pd catalysts was lower by a factor of 1.5–1.8, whereas the activity of Ni and W catalysts was lower by a factor of 2.9–4.8. The activity of sulfide catalysts based on other supports changed in approximately the same order. However, differences in *AKA* were somewhat higher than on Al_2O_3: up to one order of magnitude.

The nature of the support affected the activity of diethyl disulfide hydrogenation catalysts. Sulfide catalysts based on Al_2O_3 were found most active. The weakest dependence of *AKA* on the nature of the support was observed for Rh catalysts: the activity of Rh on SiO_2, C, and AlSi was lower than that on Al_2O_3 by a factor of only 1.2–1.6. The activity of Ni, Ru, and W sulfides on SiO_2, AlSi, and C was lower than that on Al_2O_3 by a factor of 1.2–3.0. The activity of Pd/Al_2O_3 in diethyl disulfide was higher than that of palladium catalysts based on AlSi, SiO_2, and C by a factor of 3.2–6.1. The activity of molybdenum catalysts on various supports can differ by a factor of 5.5–8.3.

In a number of hydrogenation processes, bimetallic catalysts are superior to monometallic catalysts. Therefore, we examined the hydrogenation of diethyl disulfide in the presence of bimetallic sulfide catalysts

Table 2. Specific rate and selectivity of the catalytic conversion of diethyl disulfide at x = 50% and C_0 = 1.3 vol % in helium and hydrogen atmospheres

Sulfide catalyst	Helium		Hydrogen	
	w_{sp}, mmol (g Cat)$^{-1}$ h^{-1}	S, %	w_{sp}, mmol (g Cat)$^{-1}$ h^{-1}	S, %
	T = 200°C			
Al_2O_3	0.7	67	0.7	70
$5Mo/Al_2O_3$	0.5	65	14.7	100
$5Pd/Al_2O_3$	1.2	56	6.3	98
$5Rh/Al_2O_3$	2.4	67	9.8	99
$10Ru/Al_2O_3$	2.5	55	12.7	98
2.5Ni, $10Mo/Al_2O_3$	1.1	53	26.3	96
	T = 250°C			
Al_2O_3	2.8	60	2.3	56
$5Mo/Al_2O_3$	2.7	57	14.7	80
$5Pd/Al_2O_3$	2.4	64	39.0	86
$5Rh/Al_2O_3$	4.5	68	39.0	80

(Table 4). The preparation procedure affected the *AKA* of bimetallic catalysts in diethyl disulfide hydrogenation. Thus, the activity of a catalyst prepared by the combined supporting of Ni and Mo was 1.5 times higher than the activity of a catalyst prepared by successive supporting. The activity of Ni and Mo sulfide catalysts depended on the nature of the support: the highest activity was on Al_2O_3, whereas the activity on AlSi was lower by a factor of 3.3, and that on SiO_2 and the carbon support was lower by a factor of 17. The *AKA* of the NiMo/Al_2O_3 catalyst in the diethyl disulfide hydrogenation to ethanethiol was higher than the sum of *AKA* of the monometallic catalysts Ni/Al_2O_3 + Mo/Al_2O_3 by a factor of 1.2–1.3. The initial activity of the bimetallic sulfide catalyst (Ni,Mo)/Al_2O_3 increased by a factor of 1.7 after the additional reduction with hydrogen at $T = 200°C$; however, it rapidly decreased in the course of reaction. For the other tested bimetallic catalysts (Co,Mo)/Al_2O_3, (Ni,W)/Al_2O_3, and (Pd,W)/Al_2O_3, the sum of *AKA* of the monometallic catalysts Ni (Co,Pd) + Mo (W) on the supports was equal to or higher than the activity of corresponding bimetallic catalysts. Thus, bimetallic catalysts have no advantages over monometallic catalysts in the selective hydrogenation of diethyl disulfide.

A change in the activity of sulfide catalysts depending on the nature of the support is not associated with a change in the dispersity of a metal sulfide. For example, the specific surface area of PdS on a carbon support is equal to 280 m^2/g, whereas it is ~220 m^2/g on the other supports [5]. At the same time, the catalysts on different supports differed in activity by a factor of 3–6. According to Manuilova *et al.* [6], the particle size of MoS_2 increases in the following order of supports: $C < SiO_2 < Al_2O_3$. However, the activity of Mo/Al_2O_3 in diethyl disulfide hydrogenation was higher than that of the catalyst supported on C or SiO_2. A decrease in the Mo content on Al_2O_3 from 19.5 to 5.0 wt % had no effect on *AKA*.

The acidity of support surfaces has no effect on the activity of the catalysts. AlSi exhibits the highest Brønsted acidity: the proton affinity $PA^a \cong 1200$ kJ/mol, as found from the adsorption of pyridine or ammonia; weaker proton centers occur at the surfaces of SiO_2 and Al_2O_3 with $PA^a = 1390$ and 1420 kJ/mol, respectively [7]. At the same time, the *AKA* of metal sulfides on Al_2O_3 is higher than that on AlSi by a factor of 1.2–7.5 (Table 3). The addition of 1.2 wt % *para*-toluenesulfonic acid (a strong protic acid) to the catalyst 5Pd/Al_2O_3 had almost no effect on the catalyst activity. It may be suggested that the increased activity of aluminum oxide catalysts is associated with the participation of the support in the process because pure Al_2O_3 exhibited higher activity than other supports (higher than that of AlSi by a factor of ~5 and of SiO_2 and the carbon support by a factor of 20–30). However, the rate of diethyl disulfide conversion on Al_2O_3 was considerably (by a factor of 4–10) lower than that in the presence of sulfide catalysts prepared on its basis, whereas Rh, Ru, Ni, and

Table 3. Effect of the nature of the support on the activity of monometallic sulfide catalysts in diethyl disulfide hydrogenation at $T = 200°C$

Metal sulfide*	k, l gas (g-atom M)$^{-1}$ s^{-1}			
	Supports			
	Al_2O_3	C	AlSi	SiO_2
Rh	14.3	11.3	9.1	12.3
Ru	9.2	5.5	3.3	5.4
Mo	8.3	1.5	1.1	1.0
Pd	8.1	1.1	2.1	1.5
Ni	5.0	2.6	2.9	1.2
W	3.0	1.0	1.3	2.4

* Metal contents of the sulfide catalysts (wt %): 5–19.5 (Mo), 18 (W), 5–20 (Re), 10 (Ru), and 5 (Pd, Rh and Ni).

Table 4. Activity of monometallic and bimetallic sulfide catalysts in diethyl disulfide hydrogenation at $T = 200°C$

Catalyst	AKA	
	total monometallic catalysts**	bimetallic catalysts***
(2.5Co, 10Mo)/Al_2O_3	20.4	6.2
(2.5Ni, 9.1W)/$Al_2O_3^*$	6.6	5.1
(5Pd, 18W)/$Al_2O_3^*$	9.7	5.8
(2.5Ni, 10Mo)/Al_2O_3	13.3	15.7
(2.5Ni, 10Mo)/$Al_2O_3^*$	13.3	10.3
(5Ni, 20Mo)/Al_2O_3	13.3	8.8
(1.1Ni, 5Mo)/Al_2O_3	12.2	14.5
(1.1Ni, 10Mo)/Al_2O_3	13.0	2.2
(2.5Ni, 10Mo)/AlSi	4.0	4.8
(2.5Ni, 10Mo)/SiO_2	2.2	0.9
(2.5Ni, 10Mo)/C	4.1	0.9

* Catalysts were prepared by the successive supporting of components; the other catalysts were prepared by combined supporting.

** The sum of k (l gas (g-atom M)$^{-1}$ s^{-1}) of the supported monometallic catalysts Co (Ni or Pd)/support + Mo (W)/support.

*** k per mole of total metals (l gas (g-atom ΣM)$^{-1}$ s^{-1}).

W sulfides on Al_2O_3 were more active than on the other supports by a factor of only 1.2–3.1. However, it could not be excluded that the presence of Lewis acid sites on the support surface had an effect on the activity of aluminum oxide catalysts; the Lewis acid sites participated in the activation of diethyl disulfide to increase the rate of hydrogenation. Strong Lewis acid sites with heats of CO adsorption (Q_{CO}) equal to 34 and 41 kJ/mol occur on the surface of Al_2O_3. Stronger sites with Q_{CO} = 56 kJ/mol occur on the surface of AlSi, albeit in a low concentration, whereas SiO_2 and the carbon support have no Lewis acid sites [7]. At the same time, the sulfides of some metals (Rh, Ru, Ni, and W) supported on C and SiO_2 exhibit relatively high activity in diethyl disulfide hydrogenation.

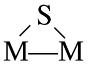
The catalyst activity depended on the activation conditions (Table 5). The catalysts prepared by sulfidization with a mixture of 15% H_2S + 85% H_2 and additionally reduced with hydrogen at T = 200°C for 0.5 h exhibited higher *AKA* than the catalysts sulfidized in a helium atmosphere and not reduced with hydrogen. However, it is highly probable that the latter were partially reduced at T = 200°C under conditions of the experiments. For example, the activity of an Ru catalyst decreased in the case of a longer reduction at T = 200°C. An increase in the reduction temperature of Ru and Mo catalysts up to T = 300–400°C also decreased the catalyst activity. These results suggest that the activity of the tested catalysts in the selective hydrogenation of diethyl disulfide to ethanethiol increases with increasing sulfide sulfur content of the catalyst and upon the partial reduction of a metal sulfide.

The preparation of the tested sulfide catalysts included their treatment with H_2S at elevated temperatures in the presence of H_2 and then the additional reduction with hydrogen. The S : M atomic ratios in these catalysts were lower than the stoichiometric values: they were 1.2–1.3, 1.4–1.6, 0.6–0.8, 0.8–1.0, 1.6–1.8, and 1.3–1.6 for Rh^{3+}, Ru^{4+}, Pd^{2+}, Ni^{2+}, Mo^{4+}, and W^{4+}, respectively. This fact may indicate that metal sulfides underwent partial reduction in the course of catalyst preparation. It is likely that in this case coordinatively unsaturated transition metal ions appeared at the surface [8].

It was found [9–11] using Ru catalysts as an example that either the heterolytic decomposition of hydrogen (with the formation of surface-bound SH groups and hydride ions) or the homolytic decomposition of hydrogen primarily occurs during the chemisorption of hydrogen depending on the S : Ru atomic ratio in the catalyst. The participation of surface protons and hydride ions in the hydrogenolysis of thiophene in the presence of Mo and Re sulfides supported on Al_2O_3 was suggested [12]. Calais *et al.* [13], who studied the liquid-phase hydrogenation of diphenyl disulfide into thiophenol in the presence of Rh, Ru, Mo, CoMo, NiMo, and NiW sulfides supported on Al_2O_3, assumed the same mechanism. They believed that, during the adsorption of diphenyl disulfide on a partially reduced metal sulfide, one sulfur atom of the disulfide forms a hydrogen bond with the proton of a surface SH group, and the other sulfur atom reacts with the hydride ion. The degradation of this surface structure results in two

Table 5. Effect of the conditions of catalyst activation on the activity in diethyl disulfide hydrogenation

Sulfide catalyst	Precursor	Sulfidization conditions	Hydrogen reduction conditions H_2	AKA, l (g-atom M)$^{-1}$ s^{-1}
$5Rh/Al_2O_3$	$RhCl_3/Al_2O_3$	H_2S + He, 150°C, 2 h	–	3.8
		H_2S + H_2, 150°C, 1 h	200°C, 0.5 h	14.3
$18W/SiO_2$	$(NH_4)_6W_7O_{24}/SiO_2$	H_2S + He, 300°C, 2 h	–	1.1
		H_2S + H_2, 300°C, 1 h	200°C, 0.5 h	2.4
$5Ni/Al_2O_3$	$NiCl_2/Al_2O_3$	H_2S + He, 250°C, 2 h	–	3.8
		H_2S + H_2, 250°C, 1 h	200°C, 0.5 h	5.0
$5Pd/Al_2O_3$	$PdCl_2/Al_2O_3$	H_2S + He, 150°C, 1 h	–	3.0
		H_2S + H_2, 150°C, 1 h	–	5.1
		H_2S + H_2, 150°C, 1 h	200°C, 0.5 h	8.1
$10Ru/Al_2O_3$	$RuCl_3/Al_2O_3$	H_2S + He, 400°C, 2 h	–	5.3
		H_2S + H_2, 150°C, 1 h	200°C, 0.5 h	9.2
		H_2S + He, 400°C, 2 h	200°C, 2 h	5.1
		H_2S + He, 400°C, 2 h	300°C, 2 h	3.6
$10Mo/Al_2O_3$	$(NH_4)_6Mo_7O_{24}/Al_2O_3$	H_2S + He, 400°C, 2 h	–	4.5
		H_2S + H_2, 400°C, 2 h	200°C, 0.5 h	8.3
		H_2S + H_2, 400°C, 2 h	–	3.5
		H_2S + H_2, 400°C, 2 h	400°C, 0.5 h	2.0

thiol molecules, the liberation of coordinatively unsaturated metal cations, and the formation of M=S or  groups. We cannot rule out that the catalytic reaction of diethyl disulfide hydrogenation to ethanethiol occurs by the mechanism proposed for diphenyl disulfide hydrogenation, because catalysts sulfidized in the absence of hydrogen exhibited noticeable activity (Table 5). However, it is well known [14–16] that the complexation of organic disulfides with protons or metal cations involves only one sulfur atom. The interaction of this atom with a proton (in solution [15, 16] or on a surface, for example, on SiO_2 [17]) results in a weak hydrogen bond, which causes only the polarization and activation of the S–S bond of a disulfide. A stronger bond appears when a disulfide sulfur atom is coordinated with electron-acceptor centers (for example, in solutions with Al, B, Ga, and Sn halides or Co, Fe, Ni, Ru, Pd, and Pt complexes [14, 18–22]). Because of this, the homolytic cleavage of the S–S bond with the formation of thiolates occurs even at room temperature. A similar phenomenon was also detected on the coordination of a disulfide with solid catalysts, such as Ni, Cu, and Fe metals or Al, Mn, and V oxides under mild conditions [17, 23–26]. It is believed that, on a partially reduced metal sulfide, diethyl disulfide is coordinated with cations. Then, it undergoes degradation at the S–S bond with the formation of surface thiolates, and the interaction of the thiolates with hydrogen atoms resulted in thiols. We found (Table 2) that ethanethiol is formed in the reaction of diethyl disulfide in the absence of hydrogen, although the rate and selectivity of this reaction are lower than in the hydrogenation.

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