

# Hydrogenolysis of Dimethyl Disulfide in the Presence of Bimetallic Sulfide Catalysts

A. V. Mashkina and L. N. Khairulina

*Boriskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

*e-mail: amash@catalysis.nsk.su*

Received June 30, 2005

**Abstract**—The hydrogenolysis of dimethyl disulfide in the presence of Ni,Mo and Co,Mo bimetallic sulfide catalysts was studied at atmospheric pressure and  $T = 160\text{--}400^\circ\text{C}$ . At  $T \leq 200^\circ\text{C}$ , dimethyl disulfide undergoes hydrogenolysis at the S–S bond, yielding methanethiol in 95–100% yield. The selectivity of the reaction decreases with increasing residence time and temperature due to methanethiol undergoing condensation to dimethyl disulfide and hydrogenolysis at the C–S bond to yield methane and hydrogen sulfide. The specific activity of the Co,Mo/Al<sub>2</sub>O<sub>3</sub> catalyst in hydrogenolysis at the S–S and C–S bonds is equal to or lower than the total activity of the monometallic catalysts. The Ni,Mo/Al<sub>2</sub>O<sub>3</sub> catalyst is twice as active as the Ni/Al<sub>2</sub>O<sub>3</sub> + Mo/Al<sub>2</sub>O<sub>3</sub> or the cobalt–molybdenum bimetallic catalyst.

**DOI:** 10.1134/S0023158407010168

## INTRODUCTION

Supported Co(Ni) and Mo(W) bimetallic sulfide catalysts are widely used in the hydrogenation of unsaturated compounds and in the hydrogenolysis of organic sulfur-containing compounds at the C–S bond (see, e.g., [1, 2]) and often exceed monometallic systems in activity. For instance, in the hydrogenolysis of thiophene to hydrogen sulfide and hydrocarbons, the activity of the Ni(Co) and Mo(W) sulfide catalysts per sum of metal g-atoms is 3–7 times higher than the total atomic activity of the supported monometallic catalysts. For benzene hydrogenation, this difference is two orders of magnitude [3, 4].

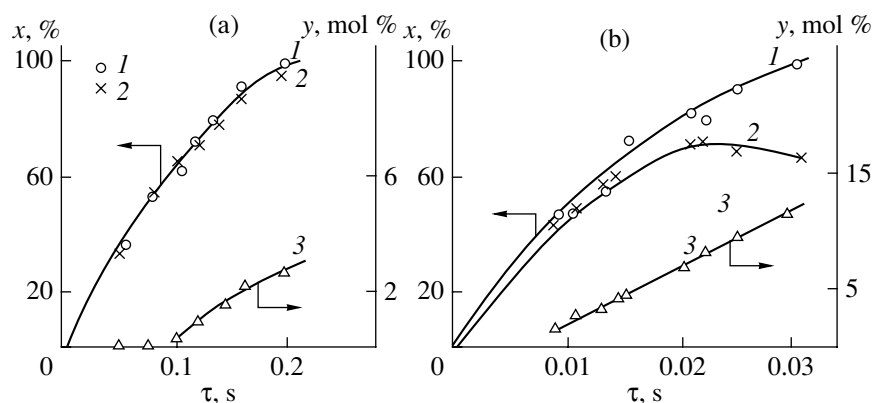
Under the action of monometallic and bimetallic sulfide catalysts, dialkyl disulfides can undergo hydrogenolysis either with C–S bond cleavage to yield H<sub>2</sub>S and a hydrocarbon or with S–S bond cleavage to yield an alkanethiol. For example, in the presence of an alumina-supported molybdenum or cobalt–molybdenum catalyst in a flow reactor at  $P = 2\text{--}5$  MPa and  $T = 375\text{--}510^\circ\text{C}$ , diethyl and dioctyl disulfides undergo deep hydrogenolysis to H<sub>2</sub>S and the respective hydrocarbon. The yield of the latter can be as high as 100%. Under static conditions (at  $P = 7\text{--}8$  MPa and  $T = 230^\circ\text{C}$ ), in the presence of molybdenum disulfide, diethyl disulfide decomposes within 2 h to ethanethiol and diethyl sulfide in yields of 13 and 10%, respectively, evolving H<sub>2</sub>S and ethane [5]. The hydrogenolysis of diethyl disulfide with S–S bond cleavage and ethanethiol formation was reported to occur under the action of several Ni(Co) and Mo(W) bimetallic sulfide catalysts on different supports (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, aluminosilicate, carbon) under atmospheric pressure and  $T = 200^\circ\text{C}$  [6]. The specific activity (reaction rate constant per g-atom of metal) of

the monometallic sulfide catalysts Ni(Co)/support + Mo/support was approximately equal or even exceeded the activity of the corresponding bimetallic catalyst. At  $P = 0.1$  MPa,  $T = 200^\circ\text{C}$ , and H<sub>2</sub> : dimethyl disulfide (DMDS) = 2 : 1 mol/mol in a nitrogen-diluted mixture, DMDS is converted into methanethiol (MT) and dimethyl sulfide (DMS) [7]. The rate of DMDS conversion per gram of the 2.4Ni(Co),9.3Mo/Al<sub>2</sub>O<sub>3</sub> catalyst is 1.1–1.7 times higher than the total reaction rate on the corresponding monometallic catalysts. However, the bimetallic catalyst is inferior to the monometallic catalysts in activity calculated per g-atom of the sum of metals. We found previously that the selective hydrogenolysis of dimethyl and diethyl disulfides to alkanethiols occurs at atmospheric pressure and  $T \geq 200^\circ\text{C}$  in the presence of Ni, Co, Rh, Ru, and Pd sulfides supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, or carbon [6, 8–10]; Co and Rh sulfides supported on alumina were the most active. The hydrogenolysis of DMDS in the presence of bimetallic sulfide catalysts was not studied.

In the present work, in order to find more active catalysts for the selective hydrogenolysis of DMDS to MT, we studied the reaction in the presence of Ni(Co),Mo/Al<sub>2</sub>O<sub>3</sub> bimetallic sulfide catalysts with various compositions and compared these catalysts with monometallic sulfide catalysts.

## EXPERIMENTAL

Catalysts were prepared by the incipient-wetness impregnation of the support (alumina,  $S_{sp} = 240$  m<sup>2</sup>/g) with aqueous solutions of appropriate compounds followed by thermal treatment. Nickel (cobalt) nitrates or chlorides and ammonium heptamolybdate (HMo) or



**Fig. 1.** Effect of the residence time on (1) the DMDS conversion and on the yields of (2) MT and (3) DMS in the presence of the 3.6Ni, 12.8Mo/Al<sub>2</sub>O<sub>3</sub> sulfide catalyst at  $T =$  (a) 160 and (b) 250°C.

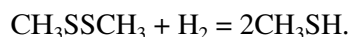
phosphomolybdic acid (PMo) were used as precursors to prepare the monometallic catalysts. Ni(Co),Mo/Al<sub>2</sub>O<sub>3</sub> bimetallic catalysts were prepared by the impregnation of alumina with solutions containing a mixture of nickel (cobalt) nitrate or chloride and HMo or PMo or by successive impregnation: the support was impregnated with a solution of nickel (cobalt) nitrate or chloride, dried, and then impregnated with a solution of HMo or PMo. After impregnation, all samples were stored in air at room temperature for 12 h and dried at 110°C (5 h). After drying, the samples based on nickel (cobalt) nitrates and most of the HMo-based samples were calcined at  $T = 500^\circ\text{C}$  for 5 h in a flow of purified dry air. Before activity measurements, the catalysts were treated with a mixture of 15% H<sub>2</sub>S + 85% H<sub>2</sub> (1 h) at  $T = 400^\circ\text{C}$  and then with hydrogen (30 min) at the measurement temperature. In the text and tables, the number before the symbol of an element is the concentration of the element (wt %). The BET specific surface area of the sulfide catalysts was 180–220 m<sup>2</sup>/g, depending on their composition. Dimethyl disulfide was reagent grade.

Catalytic experiments were carried out at atmospheric pressure, an initial DMDS concentration of  $1.6 \pm 0.1$  vol %, and  $T = 160\text{--}400^\circ\text{C}$  in a flow reactor connected to a chromatograph. Hydrogen from a cylinder was passed through a temperature-controlled bubbler filled with DMDS and was then fed into the heated reactor filled with a catalyst. After 0.5 h, the initial mixture and reaction products were sampled at intervals to be analyzed on an LKhM-8MD chromatograph with a thermal-conductivity detector (2 m  $\times$  3 mm column packed with Porapak Q + Porapak R (1 : 1); helium as the carrier gas). A fresh catalyst sample with a particle size of 0.25–0.5 mm was used in each experiment. The residence time ( $\tau$ , s) was taken to be equal to the ratio of the catalyst volume (cm<sup>3</sup>) to the gas flow rate (cm<sup>3</sup>/s) at room temperature and atmospheric pressure. From chromatographic data, we derived the DMDS conversion ( $x$ , %), product yields ( $y$ , mol %), the MT selectivity ( $S$ , %) (equal to  $y/x$ ), the rate of DMDS conversion or methane forma-

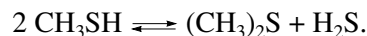
tion per gram of catalyst ( $w$ , mmol h<sup>-1</sup> (g Cat)<sup>-1</sup>, and the specific (atomic) activity of the catalyst (ACA) as the reaction rate constant per g-atom of metal ( $k$ , l<sub>g</sub> s<sup>-1</sup> (g-at M)<sup>-1</sup>) or the sum of the metals ( $k$ , l<sub>g</sub> s<sup>-1</sup> (g-at  $\Sigma$ M)<sup>-1</sup>).

## RESULTS AND DISCUSSION

To show high activity in DMDS hydrogenolysis, all catalysts needed to be pretreated with hydrogen sulfide at  $T = 400^\circ\text{C}$  and then with hydrogen at the measurement temperature. The DMDS conversion rate in the presence of the samples that were only reduced with hydrogen but not sulfurized is  $\sim 3$  times lower. Hydrogenolysis reactions in the presence of the monometallic and bimetallic catalysts proceed in the same way. At  $T \leq 200^\circ\text{C}$ , DMDS hydrogenolysis occurs mainly via S–S bond cleavage to yield methanethiol:



At a constant temperature and initial DMDS concentration, lengthening the residence time results in an increase in the DMDS conversion and MT yield (Fig. 1, Table 1). Up to  $x = 60\text{--}80\%$ , the MT selectivity is  $\sim 100\%$  and somewhat decreases at higher DMDS conversion values. The reaction products contain DMS and H<sub>2</sub>S, whose yields are approximately equal. Probably, the condensation of MT occurs:



This MT condensation reaction is favored by increasing  $\tau$  and temperature [11]. At 220–250°C, the residence time necessary for DMDS hydrogenolysis is much shorter, the DMS and H<sub>2</sub>S yields are higher, and the MT selectivity is lower than the same parameters at  $T \leq 200^\circ\text{C}$  (Figs. 1, 2). The  $\log 1/(1-x)$  value increases linearly with increasing  $\tau$  (Fig. 3), indicating that the reaction is first-order. (The catalysts containing Ni (Co) were prepared from nitrates; the Mo catalysts were prepared from HMo, except for catalysts 1 and 8, which were prepared from PMo. All of the catalysts were examined at  $T = 190^\circ\text{C}$ , except for catalyst 5, for which

**Table 1.** Effect of the residence time on the conversion of dimethyl disulfide and on the yields of the products in the presence of the sulfide catalysts at  $T = 190^\circ\text{C}$ 

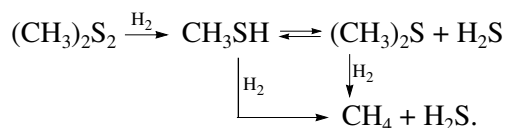
Catalyst	$\tau$ , s	$x$ , %	Yield, mol %		$S$ , %
			MT	DMS*	
10Mo/Al <sub>2</sub> O <sub>3</sub> **	0.15	46	45	0.2	98
	0.24	77	72	2.0	95
	0.38	97	90	2.9	93
2.5Ni/Al <sub>2</sub> O <sub>3</sub>	1.56	55	54	0.3	98
	2.50	74	67	3.2	91
	3.80	95	70	12.3	74
2.5Co/Al <sub>2</sub> O <sub>3</sub>	0.42	62	62	0	100
	0.60	86	84	0.5	98
	0.82	98	95	1.5	97
2.5Co,10Mo/Al <sub>2</sub> O <sub>3</sub>	0.09	50	49	0	98
	0.17	74	73	0.2	99
	0.25	96	88	3.7	92
2.5Ni,10Mo/Al <sub>2</sub> O <sub>3</sub>	0.06	55	54	0.8	98
	0.11	84	81	1.5	96
	0.14	97	90	3.0	93
5Ni,10Mo/Al <sub>2</sub> O <sub>3</sub>	0.05	45	44	0.3	98
	0.14	86	82	2.2	95
	0.19	96	87	4.4	91
3.6Ni,12.8Mo/Al <sub>2</sub> O <sub>3</sub>	0.04	63	63	0	100
	0.07	86	85	0.2	99
	0.09	97	95	0.9	98

\*Hereafter, only the DMS yield is given; its value coincided with the H<sub>2</sub>S yield within the experimental error.

\*\*This catalyst was prepared from PMo, and the other catalysts were prepared from HMo and nickel (cobalt) nitrates.

$T = 220^\circ\text{C}$ .) The hydrogenolysis rate constants increase as the temperature is raised from 160 to  $250^\circ\text{C}$ . It was found from the Arrhenius plot of the rate constant for the 5Ni,20Mo/Al<sub>2</sub>O<sub>3</sub> catalyst that the apparent activation energy of DMDS hydrogenolysis to MT is  $45 \pm 2$  kJ/mol.

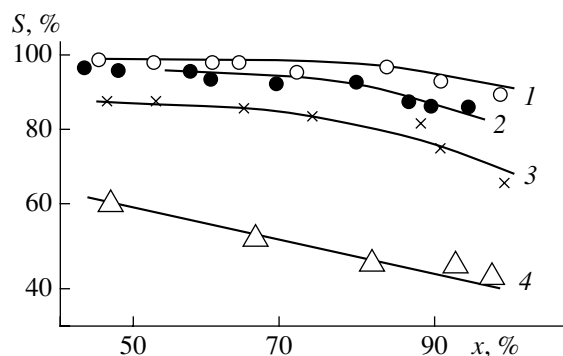
An increase in temperature to  $360\text{--}400^\circ\text{C}$  results not only in DMDS decomposition via S–S bond cleavage with the formation of MT and DMS but also in deep hydrogenolysis with C–S bond cleavage and CH<sub>4</sub> and H<sub>2</sub>S evolution (Table 2, Figs. 2, 4). Based on these results, it can be assumed that consecutive reactions occur at elevated temperatures: DMDS undergoes hydrogenolysis via S–S bond cleavage, and then the resulting MT and DMS undergo hydrogenolysis via C–S bond cleavage:



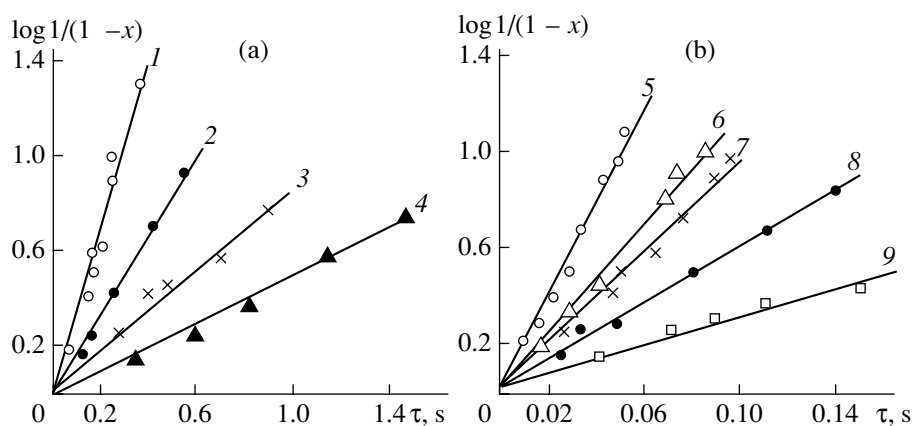
Of course, it cannot be ruled out that the C–S bond dissociates immediately in DMDS, but even if this is the case, the contribution from this reaction to the over-

all hydrogenolysis process is small, because methane and hydrogen sulfide begin to form at a noticeable rate at a DMDS conversion above 80%.

For a quantitative comparison between catalytic activities, we calculated  $w$  (at  $x = 60\%$  and  $S \sim 100\%$ ) and ACA. The activity of the catalysts in DMDS hydro-



**Fig. 2.** MT selectivity versus DMDS conversion for the 3.6Ni,12.8Mo/Al<sub>2</sub>O<sub>3</sub> sulfide catalyst at (1) 160, (2) 220, and (3)  $250^\circ\text{C}$ . (4) The same for the 2.5Co,10Mo/Al<sub>2</sub>O<sub>3</sub> catalyst at  $T = 380^\circ\text{C}$ .



**Fig. 3.** Plot of  $\log 1/(1-x)$  versus residence time in the hydrogenolysis of DMDS to MT in the presence of (a) monometallic and (b) bimetallic sulfide catalysts. The active component content of  $\text{Al}_2\text{O}_3$ : (1, 2) 20Mo, (3) 2.5Co, (4) 5Ni, (5, 6) 3.6Ni, 12.8Mo, (7, 8) 2.5Ni, 10Mo, and (9) 2.5Co, 10Mo.

genolysis with S–S bond cleavage and MT formation at  $T \leq 200^\circ\text{C}$  depends on the catalyst composition, the preparation method, the nature of the precursor of the active component, and thermal treatment conditions (Table 3).

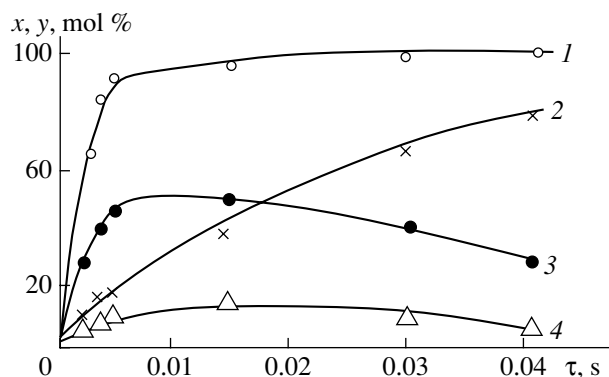
The nature of the precursor (chloride or nitrate) has no effect on the activity of the  $\text{Ni}(\text{Co})/\text{Al}_2\text{O}_3$  monometallic sulfide catalysts in hydrogenolysis at the S–S bond. However, the “nitrate” samples have to be calcined at  $T = 500^\circ\text{C}$  before sulfurization, while the “chloride” samples need only drying. For the  $10\text{Mo}/\text{Al}_2\text{O}_3$  sulfide catalyst prepared using PMo,  $w$  is 1.7 times higher than  $w$  for the sample prepared from HMo. The activity of the  $20\text{Mo}/\text{Al}_2\text{O}_3$  catalyst depends on the nature of the precursor to a lesser extent.

For the  $\text{CoMo}/\text{Al}_2\text{O}_3$  bimetallic sulfide catalysts prepared from HMo and cobalt nitrate, the rate of DMDS hydrogenolysis at the S–S bond is  $\sim 1.4$  times higher than that for the samples prepared from HMo and cobalt chloride. The  $\text{Ni,Mo}/\text{Al}_2\text{O}_3$  catalysts prepared from PMo and nickel nitrate are  $\sim 1.3$  times more active than the samples prepared from HMo and nickel chloride. The activity of the bimetallic catalysts prepared by simultaneous loading with Ni and Mo is equal to or higher than the activity of the catalysts prepared by successive loading with the metals.

The activity of the catalysts depends substantially on the active component content of the support. The hydrogenolysis rate increases by a factor of  $\sim 3$  as the Ni content of  $\text{Al}_2\text{O}_3$  is increased from 2.5 to 10 wt %,

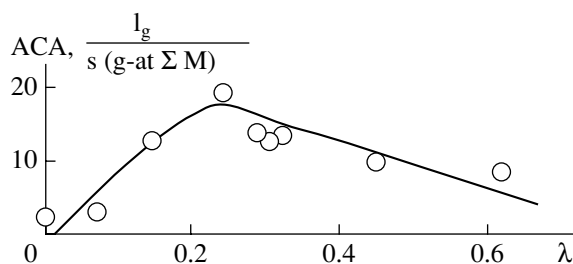
**Table 2.** Hydrogenolysis of dimethyl disulfide at 360 and  $400^\circ\text{C}$

Catalyst	$T, ^\circ\text{C}$	$\tau, \text{s}$	$x, \%$	Yield, mol %			$w$ in terms of $\text{CH}_4$ , $\text{mmol h}^{-1} (\text{g Cat})^{-1}$	$k$ , in terms of $\text{CH}_4$ , $\text{l}_\text{g} \text{s}^{-1} (\text{g-at } \Sigma \text{M})^{-1}$
				MT	DMS	$\text{CH}_4$		
2.5Co/ $\text{Al}_2\text{O}_3$	380	0.012	93	60	27	6	167	15.8
	380	0.024	100	49	33	16	21	22.5
	400	0.014	97	52	22	10	23.3	23.0
10Mo/ $\text{Al}_2\text{O}_3$	380	0.015	94	44	19	23	57	26.1
	380	0.035	98	37	16	47	50	27.2
	380	0.058	100	22	12	70	45	31.1
	380	0.625	100	0	0	100	—	—
	400	0.018	98	40	12	35	73	35.8
	400	0.625	100	0	0	100	—	—
	400	0.018	98	40	12	35	73	35.8
2.5Co, 10Mo/ $\text{Al}_2\text{O}_3$	360	0.005	79	40	10	10	56	18.7
	380	0.004	93	46	10	18	140	43.9
	380	0.041	100	26	5	81	—	—
	400	0.005	99	12	8	31	192	65.7
	400	0.041	100	29	3	72	—	—
	400	0.041	100	29	3	72	—	—



**Fig. 4.** DMDS hydrogenolysis at the C–S bond on the 2.5Co,10Mo/Al<sub>2</sub>O<sub>3</sub> sulfide catalyst at  $T = 380^\circ\text{C}$  and various residence times: (1) DMDS conversion, (2) methane yield, (3) MT yield, and (4) DMS yield.

although the ACA value remains unchanged within the experimental accuracy. An increase in the Co content of Al<sub>2</sub>O<sub>3</sub> from 2.5 to 8 wt % increases the reaction rate by a factor of 1.5–2 and decreases the ACA value by a factor of 1.4–2.7, depending on the nature of the precursor. As the Mo content of Al<sub>2</sub>O<sub>3</sub> increases from 10 to 20 wt %,  $w$  increases by a factor of 1.3 for the samples prepared from HMo and remains invariable for the samples prepared from PMo. ACA decreases by a factor of 1.6–2.1 in both cases, probably because of a decrease in the extent of dispersion of the metallic components. Furthermore, the activity of the bimetallic catalysts depends on the proportions of the supported met-



**Fig. 5.** Specific activity of Ni,Mo/Al<sub>2</sub>O<sub>3</sub> bimetallic sulfide catalysts at  $T = 190^\circ\text{C}$  versus Ni/(Ni + Mo) atomic ratio ( $\lambda$ ).

als. For instance, the specific activity of the alumina-supported nickel–molybdenum catalysts depends on the atomic ratio  $\lambda = \text{Ni}/(\text{Ni} + \text{Mo})$ : it is higher at  $\lambda = 0.2\text{--}0.3$  than at  $\lambda = 0.4\text{--}0.6$  or at  $\lambda < 0.2$  (Fig. 5). Similar regularities are observed for thiophene hydrogenolysis [1–4].

Our experiments showed that the specific activity of the sulfide catalysts depends on the nature of the active component. For example, the monometallic cobalt catalysts surpass the nickel and cobalt catalysts in the ACA value by a factor of 2–2.5. At a given supported metal content, the Ni,Mo/Al<sub>2</sub>O<sub>3</sub> sulfide catalysts are at least twice more active in DMDS hydrogenolysis at the S–S bond than CoMo/Al<sub>2</sub>O<sub>3</sub> (Tables 3, 4). A comparison between the ACA values of the monometallic and bimetallic catalysts (Table 4) shows that, in the hydrogenolysis of DMDS to MT, the Ni,Mo/Al<sub>2</sub>O<sub>3</sub> bimetallic sulfide systems are approximately twice as active as Ni/Al<sub>2</sub>O<sub>3</sub> + Mo/Al<sub>2</sub>O<sub>3</sub>. This is at variance with the data

**Table 3.** Rate of dimethyl disulfide conversion into methanethiol and the specific activity of the sulfide catalysts at  $T = 190^\circ\text{C}$

Metal content of Al <sub>2</sub> O <sub>3</sub>	Precursor	$w, \text{mmol h}^{-1} \times (\text{g Cat})^{-1}$	$\text{ACA}, l_g \text{ s}^{-1} \times (\text{g-at M})^{-1}$	Metal content of Al <sub>2</sub> O <sub>3</sub>	Precursor	$w, \text{mmol h}^{-1} \times (\text{g Cat})^{-1}$	$\text{ACA}, l_g \text{ s}^{-1} \times (\text{g-at } \Sigma \text{M})^{-1}$
Monometallic catalysts				Bimetallic catalysts			
2.5Ni	Ni(NO <sub>3</sub> ) <sub>2</sub>	1.2	1.8	1Ni,20Mo	Ni(NO <sub>3</sub> ) <sub>2</sub> , HMo	12.1	3.2
5Ni	Ni(NO <sub>3</sub> ) <sub>2</sub>	2.2	1.6	1.1Ni,5.8Mo	Ni(NO <sub>3</sub> ) <sub>2</sub> , HMo*	26.0	19.8
2.5Ni	NiCl <sub>2</sub>	1.5	2.2	2.1Ni,7.4Mo	Ni(NO <sub>3</sub> ) <sub>2</sub> , HMo	22.4	12.7
10Ni	NiCl <sub>2</sub>	4.3	1.6	2.5Ni,10Mo	Ni(NO <sub>3</sub> ) <sub>2</sub> , PMo	38.8	16.4
2.5Co	CoCl <sub>2</sub>	4.0	5.7	2.5Ni,10Mo	NiCl <sub>2</sub> , PMo	28.3	12.3
8Co	CoCl <sub>2</sub>	8.7	4.1	2.5Ni,10Mo	Ni(NO <sub>3</sub> ) <sub>2</sub> , HMo	28.9	12.6
2.5Co	Co(NO <sub>3</sub> ) <sub>2</sub>	4.3	6.3	5Ni,10Mo	Ni(NO <sub>3</sub> ) <sub>2</sub> , HMo	30.2	10.2
8Co	Co(NO <sub>3</sub> ) <sub>2</sub>	6.2	2.9	3.6Ni,12.8Mo	Ni(NO <sub>3</sub> ) <sub>2</sub> , HMo	40.2	13.2
10Mo	HMo	5.0	3.0	10Ni,10Mo	Ni(NO <sub>3</sub> ) <sub>2</sub> , HMo	37.7	8.7
10Mo	PMo	8.2	5.0	2.5Co,10Mo	Co(NO <sub>3</sub> ) <sub>2</sub> , HMo	20.6	8.9
20Mo	HMo	6.3	1.9	2.5Co,10Mo	CoCl <sub>2</sub> , HMo	14.6	5.7
20Mo	PMo	8.0	2.6	2.5Co,10Mo	CoCl <sub>2</sub> , HMo*	14.1	5.3

\* This catalyst was prepared by successively supporting active components, and the other catalysts were prepared by simultaneous supporting.

**Table 4.** Specific activity, in dimethyl disulfide hydrogenolysis, of the monometallic and bimetallic sulfide catalysts prepared from nickel (cobalt) nitrates and HMo

Active component content of Al <sub>2</sub> O <sub>3</sub>	T, °C	ACA		Active component content of Al <sub>2</sub> O <sub>3</sub>	ACA at T = 190°C	
		bimetallic catalysts*	monometallic catalysts**		bimetallic catalysts*	monometallic catalysts**
2.5Co,10Mo	190	8.9	9.3	2.5Ni,10Mo	12.6	7.2
	200	9.5	10.5	3.6Ni,12.8Mo	13.2	5.0
	380	43.9***	41.9	5Ni,10Mo	10.2	4.6
	400	65.7***	59.1	10Ni,10Mo	8.7	4.6

\*k per g-atom of the sum of metals ( $\text{l}_g \text{ s}^{-1} (\text{g-at } \Sigma \text{ M})^{-1}$ ).

\*\*Total k value ( $\text{l}_g \text{ s}^{-1} (\text{g-at M})^{-1}$ ) for the Co(Ni)/Al<sub>2</sub>O<sub>3</sub> + Mo/Al<sub>2</sub>O<sub>3</sub> monometallic catalysts.

\*\*\*Catalytic activity in hydrogenolysis at the C–S bond with methane and H<sub>2</sub>S formation. The other values in this column refer to hydrogenolysis at the S–S bond with MT formation.

reported for diethyl disulfide hydrogenolysis to ethanethiol [6] and with the results obtained for DMDS hydrogenolysis at a low hydrogen concentration [7]. The specific activity of the Co,Mo/Al<sub>2</sub>O<sub>3</sub> bimetallic sulfide catalysts in DMDS hydrogenolysis via S–S bond cleavage is equal to the total specific activity of the Co/Al<sub>2</sub>O<sub>3</sub> + Mo/Al<sub>2</sub>O<sub>3</sub> monometallic catalysts within the experimental error. In the deep hydrogenolysis of DMDS at the C–S bond ( $T = 360\text{--}400^\circ\text{C}$ ), the specific activity of the Co,Mo/Al<sub>2</sub>O<sub>3</sub> bimetallic sulfide catalyst is again approximately equal to the sum of the activities of the monometallic catalysts (Table 4).

Thus, as distinct from the hydrogenolysis of other sulfur-containing substances [1–4], the S–S bond cleavage in DMDS on the Ni,Mo/Al<sub>2</sub>O<sub>3</sub> bimetallic catalysts experiences only a slight synergetic effect. This effect is not observed in the case of DMDS hydrogenolysis at the S–S and C–S bonds in the presence of the Co,Mo/Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst.

Our results for DMDS hydrogenolysis cannot be explained in the framework of the concerted mechanism proposed for thiophene hydrogenolysis. In this mechanism, the main role is played by “occluded hydrogen” in the active component of the bimetallic catalyst [12]. Occluded hydrogen is present in the bimetallic sulfide catalysts and monometallic Ni/Al<sub>2</sub>O<sub>3</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> catalysts but is absent from the Co/Al<sub>2</sub>O<sub>3</sub> monometallic sulfide catalyst [13]. However, our experiments showed that the CoS/Al<sub>2</sub>O<sub>3</sub> catalyst is highly active in DMDS hydrogenolysis at both the S–S and C–S bond and its specific activity exceeds the specific activity of the Ni/Al<sub>2</sub>O<sub>3</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> catalysts containing occluded hydrogen [13]. The specific activity of the Co,Mo/Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst containing occluded hydrogen is equal to or even lower than the total activity of the Co/Al<sub>2</sub>O<sub>3</sub> + Mo/Al<sub>2</sub>O<sub>3</sub> monometallic catalysts, and the Ni,Mo/Al<sub>2</sub>O<sub>3</sub> bimetallic catalysts exhibit only a slightly higher specific activity than the Ni/Al<sub>2</sub>O<sub>3</sub> + Mo/Al<sub>2</sub>O<sub>3</sub> sulfide catalyst.

Probably, DMDS and thiophene differ in the hydrogenolysis mechanism on the bimetallic sulfide cata-

lysts, as was postulated for the same reaction on monometallic sulfide catalysts [6, 9, 10]. Contact between DMDS and the catalysts results in the formation of a surface complex in which electrons are transferred from one sulfur atom of disulfide to the transition metal ion [14, 15]. The S–S bond in disulfides is weaker than the C–S bond. For instance, the strength of the S–S bond in DMDS is 274 kJ/mol and the strength of the C–S bond in DMS is 309 kJ/mol [16]. Because of this, the surface complex of DMDS with the catalyst decomposes at the S–S bond even at low temperatures to form methyl thiolate (CH<sub>3</sub>S) surface structures [17]. The interaction of the latter with activated hydrogen produces methanethiol. At elevated temperatures, the C–S bonds in the CH<sub>3</sub>S fragments dissociate to evolve methane and H<sub>2</sub>S. These views agree with the results obtained for DMDS and MT adsorption on Mo(110) [17]. However, they undoubtedly require additional proof.

It was found previously that cobalt and rhodium sulfides supported on alumina are the most efficient catalysts in DMDS hydrogenolysis at the S–S bond [10, 18]. As compared to these catalysts, the alumina-supported nickel–molybdenum sulfide catalysts examined here show high specific activity and efficiency in methanethiol formation. This allows one to use these bimetallic catalysts in the production of methanethiol from dimethyl disulfide, which forms in abundance in the oxidative desulfurization of gases.

## REFERENCES

1. Topsøe, H., Clausen, B.S., and Massoth, F.E., *Hydrotreating Catalysis: Science and Technology*, vol. 11 of *Catalysis: Science and Technology*, Anderson, J.R. and Boudart, M., Eds., New York: Springer, 1996.
2. Navalikhina, M.D. and Krylov, O.V., *Usp. Khim.*, 1998, vol. 67, no. 7, p. 656.
3. Startsev, A.N., Shkuropat, S.A., and Bogdanets, E.N., *Kinet. Katal.*, 1994, vol. 35, no. 2, p. 282.

4. Startsev, A.N., Rodin, V.N., Aleshina, G.I., and Akse-  
nov, D.G., *Kinet. Katal.*, 1998, vol. 39, no. 2, p. 238  
[*Kinet. Catal.* (Engl. Transl.), vol. 39, no. 2, p. 221].
5. Obolentsev, R.D. and Mashkina, A.V., *Gidrogenoliz  
seraorganicheskikh soedinenii nefiti* (Hydrogenolysis of  
Organosulfur Compounds of Petroleum), Moscow:  
Gostoptekhizdat, 1961.
6. Mashkina, A.V. and Khairulina, L.N., *Kinet. Katal.*,  
2002, vol. 43, no. 2, p. 285 [*Kinet. Catal.* (Engl. Transl.),  
vol. 43, no. 2, p. 261].
7. Cadot, E., Lacroix, M., Breyse, M., and Arretz, E.,  
*J. Catal.*, 1996, vol. 164, no. 3, p. 490.
8. Mashkina, A.V., Yakovleva, V.N., Sakhaltueva, L.G., and  
Khairulina, L.N., *Neftekhimiya*, 2001, vol. 41, no. 1,  
p. 54 [*Pet. Chem.* (Engl. Transl.), vol. 41, no. 1, p. 50].
9. Mashkina, A.V. and Khairulina, L.N., *Neftekhimiya*,  
2004, vol. 44, no. 1, p. 57 [*Pet. Chem.* (Engl. Transl.),  
vol. 44, no. 1, p. 52].
10. Mashkina, A.V. and Khairulina, L.N., *Kinet. Katal.*,  
2005, vol. 46, no. 6, p. 921 [*Kinet. Catal.* (Engl. Transl.),  
vol. 46, no. 6, p. 873].
11. Mashkina, A.V. and Yakovleva, V.N., *Kinet. Katal.*,  
1997, vol. 38, no. 4, p. 591 [*Kinet. Catal.* (Engl. Transl.),  
vol. 38, no. 4, p. 541].
12. Startsev, A.N. and Zakharov, I.I., *Usp. Khim.*, 2003,  
vol. 72, no. 6, p. 579.
13. Zakharov, I.I., *Doctoral (Chem.) Dissertation*, Novosi-  
birsk: Inst. of Catalysis, 2004.
14. Ganyushina, L.A., Gur'yanova, E.N., Romm, I.P., and  
Lobanova, L.A., *Zh. Obshch. Khim.*, 1979, vol. 49, no. 9,  
p. 2090.
15. Lyapina, N.K., Lygin, V.I., and Ulendeeva, L.D., *Usp.  
Khim.*, 1980, vol. 49, no. 6, p. 998.
16. Tumanov, V.E. and Denisov, E.T., *Neftekhimiya*, 2003,  
vol. 43, no. 6, p. 406 [*Pet. Chem.* (Engl. Transl.), vol. 43,  
no. 6, p. 368].
17. Kang, D.H. and Friend, C.M., *Langmuir*, 2004, vol. 20,  
no. 26, p. 11 443.
18. RF Patent 2243819, 2005.